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EUROPEAN SHALE-TREATING PRACTICE

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BY

WILLIAM W. ODELL AND E. L. BALDESCHWIELER

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

EUROPEAN SHALE-TREATING PRACTICE[1/]

By William W. Odell[2/] and E. L. Baldeschwieler[3/]

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INTRODUCTION

In Europe and in certain other foreign countries studies have been made, extending over a period of years, relating to the winning of oil from oil shale. More work has been done in these countries than in the United States, for the reason that a supply of natural petroleum has not been so generally available there as here. Information has been obtained relating to present practices in these foreign lands in the development of a shale-oil industry. It is realized that in the past there has been very little inducement to invest capital in shale-oil enterprise in the United States because the supply of petroleum has been plentiful; however, the time possibly is not far distant when the utilization of oil shale may be considered a desirable and financially sound venture, as it may be necessary before long to augment our supply of oil with that recovered by processing shale.

The data presented herein portrays at least some of the thoughts of those engaged in obtaining oil from oil shale in Europe, and they depict some of the results thus far obtained as well as certain plans for further efforts to win oil from shale; it is hoped that those who undertake the development of a shale-treating industry in this country will find useful information in this report.

Most of the oil shales of Europe (Estonian shales excepted) may be classed as low-grade when compared with the larger deposits in the United States; hence, any processes that prove feasible in Europe, employing such shales as raw material without the protection of tariff or subsidy, should also be of interest here in the course of time.

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SUMMARY

In Europe, where petroleum is not plentifully distributed or available, particularly in Germany, France, and Estonia, efforts have been made in recent years to produce motor fuel and lubricating oil by processing oil shale.

In France and Germany the feeling among engineers and chemists working in this field is that Pumpherston retorts of the type used for many years in Scotland are not well suited to the economic treatment of the oil shales of continental Europe, and that other means and methods might prove more satisfactory.

In Germany, prior to the war, little encouragement was given to investigators in this field. Apparently, it was assumed that the Rumanian oil supply and that which seemed to be accessible through the capture of the Caucasian fields would be ample. After the Rumanian refineries had been bombed, and when the Caucasian supply was no longer available, an attempt was made to develop the oil-shale deposits of Estonia. The Russians bombed the Estonian shale-oil plants in 1940 and 1941, but the Germans rebuilt them to their original capacity of 100,000 metric tons (110,200 short tons) of oil per year and planned to expand this capacity to 1,500,000 metric tons (1,653,000 short tons) per year. The Russians took possession of these plants just a few days before they were to be put into operation. Subsequently, a feverish effort was made to utilize the low-grade oil shale of Württemberg, Germany. Construction of a number of plants for processing shale was ordered, and some were completed and in operation a few months before the end of the European war.

The following developments and plants in continental Europe are considered specifically in this report:

1. PORTLAND CEMENT WORKS AT DOTTERNHAUSEN,
(PORTLANDZEMENTWERK, DOTTERNHAUSEN, NEAR BALINGEN, WURTTEMBERG)

In this plant the oil shale was heat-treated in a Meier-Grolman retort, in which steam superheated to 800° C. in a recuperator system was passed horizontally through a downward-moving mass of crushed shale; the evolved oil vapors and gases passed out with the steam in the opposite side of the retort. As the shale had a high lime content, ground residue could be used as hydraulic lime, and some of it was marketed as such. The bulk of the shale residue was mixed with limestone and coke, and the mixture was sintered on a Dwight Lloyd Sinterband to produce a cement that was called Portland cement.

2. UNDERGROUND SHALE-TREATING PLANT AT SCHÖRZINGEN
(KOHLE-OEL UNION VON BUSSE KOMMANDITGESELLSCHAFT, SCHÖRZINGEN, WÜRTTEMBERG)

This plant heat-treated shale in underground tunnels by internal combustion methods. The oil thus recovered was appreciably less than was obtained by the laboratory Fischer-retort test. The first tunnels made were

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6.5 feet wide, 7.1 feet high, and 195 feet long. The shale roofs and parts of the walls were so broken by explosive charges that there resulted a group of tunnels filled with a porous mass of broken shale approximately 195 feet long. Each of these tunnels was sealed at one end and a coke fire was kindled at the other end to ignite the shale within the tunnel. Suction was applied at the sealed end by an exhauster, the intake of which was connected by a pipe line to the sealed end of the tunnels. The evolved gases and vapors were removed through the latter pipe; the heavy oil condensed and was drained from the system.

3. MEILER SHALE-TREATING PLANTS. PYROLYSIS OF LARGE PILES ABOVE GROUND. (DEUTSCHE OELSCHIEFER FORSCHUNG GESELLSCHAFT, SCHOMBERG, WURTTEMBERG)

This company operated a number of plants in the Balingen district. The operation was very similar to that formerly employed in carbonizing wood in large piles. The broken shale was piled in beds containing 1,500 metric tons (1,650 short tons) on top of a series of spaced pipes having slotted end sections; these pipes were connected to a gas-collecting main, which led to an exhauster. Each bed was 9.76 feet deep, 42 feet wide, and 130 feet long. A fire was kindled on the top of the pile, and the products of combustion and pyrolysis were removed as generated by the exhauster and caused to flow through a cooling system, from which the liquid products were removed. Approximately 2-1/2 days were required for the heat wave to travel through the entire bed (for complete pyrolysis of the shale). The amount of oil recovered was said to be 80 percent of that indicated by the Fischer assay test. The type of equipment required in this operation is not complex, and the whole plant can be operated with a minimum number of highly skilled persons. Of the total oil produced, 60 percent was collected from the gas-header drips and substantially all of the rest from Cottrell precipitators.

It was stated that oil could be produced at a cost (in Germany) of 227 marks per short ton from shale yielding 5 percent oil by Fischer assay. That is equivalent to 36.4 cents per U. S. gallon, allowing 40 cents as the equivalent of 1 mark.

4. PILOT-PLANT DEVELOPMENTS IN GERMANY

Pilot-plant developments and experiments have been conducted in Germany by various investigators but reference is made here to two developments in particular, because they led to the construction of commercial-size units, which were largely completed. One such unit, built at the plant of the Portlandzementwerk (Portland Cement Works), Dotternhausen, comprised a chamber for heating and circulating a liquid aluminum alloy with means for supplying crushed small-size shale to the top of said chamber and for immersing it in the liquid alloy, and having provisions for scooping or skimming off the shale residue and for separately discharging the stack gas and the products of pyrolysis. It was stated that the shale would be in contact with the metal 5 to 10 minutes, the mechanical and oxidation losses of the alloy would be very small, the yield of oil would be high as compared with the Fischer assay test, and that the capacity

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would be high with low labor costs. It has not been demonstrated that these results can be attained.

Another plant, largely constructed, is based upon the use of the Schweitzer retort, which employs the same principles of operation as the N. T. U. retort used many years ago in California. The crushed shale was to be charged into a cylindrical retort from the top to a depth of 16.5 feet, and then the shale was to be ignited at the top and the products of combustion and pyrolysis withdrawn from the bottom by an exhauster; some steam was to be used in the operation to control temperature in the shale bed. This is a batch process. The proposed operation differed from that of the N. T. U. process, in that in this case the retort was to be lifted from its base and dumped after each batch of shale was processed. The plant, which is almost completed, is at Frommern, Württemberg, and comprises 28 retorts, which are said to be sufficient for treating 1,100 short tons of shale per day, yielding 38.5 to 44 short tons of oil per day. The retort is 9.75 feet in diameter and 21 feet high and will hold 38 to 44 short tons of shale. The anticipated oil yield is said to be 85 to 90 percent of the Fischer retort yield.

Oil has not been made from shale in Germany on a cost basis that could be considered economical in the United States under prevailing conditions.

5. DEVELOPMENTS IN FRANCE

In France, interest in oil-shale utilization has been manifest for many years, although commercial developments have been small. One plant, at Autun, is operating 3 batteries of Pumpherston-type retorts, 40 retorts in each battery. Although this plant has been producing oil regularly for some time, it is evident that the industry in France will expand along other lines than by the installation of Pumpherston retorts. The capacity of the retorts now in use at Autun is 7 metric tons (7.7 short tons) of shale per day per retort, and the yield of oil is 85 percent of the Fischer assay. Developments in France have brought forth two distinctive types of retorts, which it is said have given a good account of themselves in pilot-plant tests and which will be tested very soon on a commercial scale. These retorts or systems are known as (a) the Lantz retort, as developed at St. Hilaire, and (b) the Marecaux retort, developed at Lavernhe.

The Lantz retort, shown diagrammatically in figure 7, has been operated on a pilot-plant scale (88 short tons per day) for a number of years, and one unit has been built which it is estimated will have a capacity for treating 500 metric tons (550 short tons) of shale per day. The process steps include the following: Crushed shale, 1/2- to 2-inch size, is fed into the top of the retort and passes continuously downwardly discharging at the bottom. The retort proper is rectangular in cross section and has side-wall louvres whereby hot circulating gases can be and are passed continuously through the shale bed horizontally - in through one side wall and out through the opposite wall. The circulating gas is preheated to 500° C. in a separate furnace. Ten percent of the circulating gas is withdrawn continuously for oil recovery. The upper portion of the retort, comprising a drying zone, is adapted to the passage therethrough of waste hot

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stack gases, which preheat the shale to be treated to 150° C. Water is used for quenching the spent shale as discharged, and the steam generated passes into the gas-circulating system. The yield of oil is said to be 100 percent of that shown by the Fischer retort test; in pilot-plant operations the yield was 132 pounds of oil per short ton of shale treated.

The Marecaux retort, shown diagrammatically in figure 9, treats crushed shale (1/8 to 1 inch) by passing it, with agitation, downward between two vertical concentric cylinders, as an annular column, while heat is being applied externally to the outer cylinder. Superheated steam at 400° C. is introduced into the shale in process at numerous levels for the purpose of facilitating pyrolysis. The inner cylinder has spiral members on its outer surface and rotates slowly during processing, and sealing means are provided that prevent air from entering the retort. The yield of oil obtained in pilot-scale operation was 92 percent of the Fischer assay, but there remained in the gas 8 percent of condensable vapors; hence, the total yield of liquid products obtainable is about 100 percent of the Fischer assay.

The Government of France is interested in promoting the shale-processing industry because of a deficiency in their natural petroleum resources, and it appears that in the very near future commercial-size shale-processing plants will be in operation in France that will demonstrate the relative worth and applicability of various retorts and processes for treating the oil shales in France.

6. DEVELOPMENTS IN ESTONIA

In Estonia the bituminous shales yield, by heat treatment, as much as 20 percent by weight of oil and readily condensable hydrocarbons. While the Estonian deposits were under German control an effort was made by German technologists to increase production of oil, aiming at 1,500,000 metric tons (1,653,000 short tons) of oil per year, and to refine the crude products in the interest of the war effort. In the treatment of Estonian shale, chiefly two distinct and different types of retorts were used. One, known as the Kivioli tunnel oven, uses hot circulating gases as a heating medium without the use of internal-combustion steps, thereby producing a vapor product without dilution by gaseous products of combustion. The gas evolved is insufficient to supply the heat requirements of the process. The other is known as the Pintsch retort or Pintsch generator, in which pyrolysis of the shale is accomplished by internal-heating methods; the vapors evolved are diluted with gaseous products of combustion, but an excess of gas is produced. The tunnel oven is shown in figures 15, 16, and 17; the Pintsch retort is shown in figure 11. Methods of refining and properties of the products are shown in the section designated "Shale Developments in Estonia;" flow diagrams and yields of products also are presented. The crude oils from the two different processes are not alike.

The details as to plans for Estonian development and the steps taken by the Germans were obtained from documents acquired in Germany.

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PROCESSING OIL SHALE IN EUROPE

GERMANY

In Germany there are large deposits of oil shale, particularly in Württemberg, but only in very recent years has that government been particularly interested in the recovery of oil therefrom. Dependence was put upon the supply of oil from Rumania and other sources near to Germany early in the war, and later, it appears, the conquest of the Caucasian fields was envisioned as making available an additional supply. However, after the bombing of the Rumanian refineries, and the elimination of the Caucasian oil supply, the oil shale of Estonia was looked upon as a major source of supply. The oil shale of Estonia yields, by heat treatment, approximately 20 percent by weight of oil. The Russians bombed the Estonian shale-oil plants in 1940 and 1941, but the Germans not only rebuilt them to their original capacity of 100,000 metric tons (110,200 short tons) of oil per year but had initiated plans to raise production to 1,500,000 metric tons (1,653,000 short tons) per year. The Russians took over these plants just before they were ready to be operated.

In 1943, at the order of the Reich, the Deutsche Oelschiefer Forschung Gesellschaft was formed to study the possibilities of winning oil from shale. A pilot plant was built at Schömberg near Balingen, Germany, to evaluate the various proposed processes for treating oil shale, the motive being to reduce the cost of producing oil. Before any solution for the economic problem was found, it became necessary, with the loss of Rumanian and Estonian supplies, to act and obtain oil as soon as possible from the oil shales of Württemberg; this decision was reached early in 1944. Accordingly, orders were given for the erection of a number of plants in the Balingen district. Finances, the necessary materials of construction, and labor were obtained through government aid. The results of these efforts and the anticipated results based upon pilot-plant operations follow.

Schweitzer Retort and Process

Although very little attention was given to the efforts of Dr. A. Schweitzer to develop a shale-treating process before the war, an order was given subsequently for the erection, by Lias Oelschiefer Forschung G.m.b.H., at Frommern, Württemberg, of a plant containing 28 Schweitzer retorts. This plant, which was largely completed, was rated to treat 1,100 short tons of shale and produce 38.5 to 44 short tons of oil per day. The plans contemplated subsequent expansion of the daily capacity to 2,200 short tons of shale. The inventor believed that the operation would be economical when the latter capacity was reached. Although this plant was never operated, estimated operating results were given based upon pilot-plant operation and upon experiments conducted by Dr. Schweitzer at Metzingen.

The retort, as shown in figure 1, is an open-top cylinder free of insulation or lining, 9.75 feet in diameter and 21.3 feet high, which rests in a water-seal steel base supported on a concrete foundation. A steel

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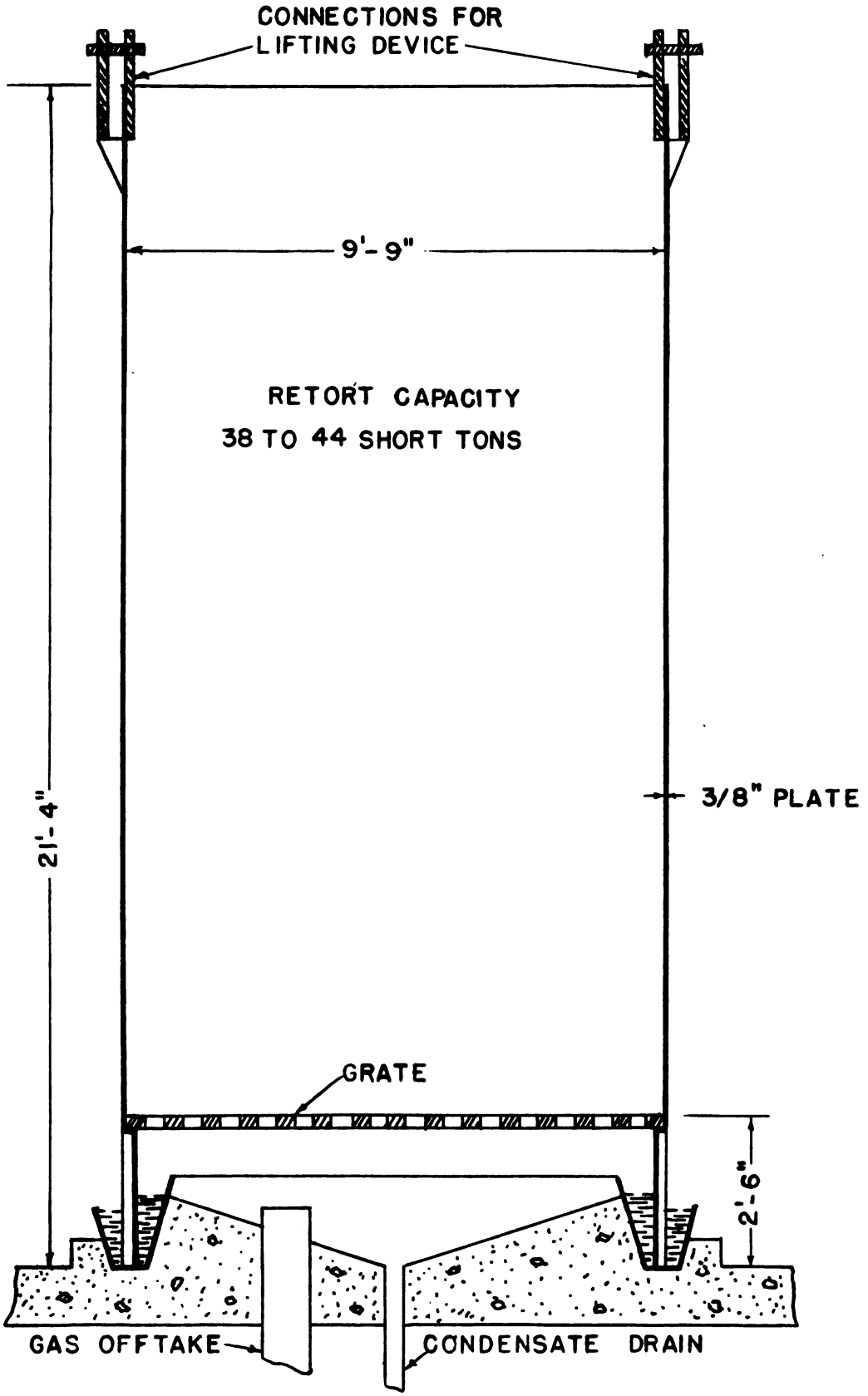

FIG. 1. DIAGRAMMATIC SECTIONAL VIEW OF A SCHWEITZER RETORT

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grid is permanently fixed within the cylinder about 2.5 feet above the bottom and functions as a grate. A drain is supplied to carry away liquid condensate from the base of the retort, and a gas offtake is provided for removing gases from beneath the shale bed. This retort, when filled with broken shale to a depth of 16.4 feet above the grid, will hold about 38 to 44 short tons. An exhauster is connected in the system to remove the gas from the retorts. There are two of these, each with a capacity of about 1,060,000 cubic feet per hour, one being a standby.

In the operation of the Schweitzer retort, crushed shale, preferably 15 to 50 mm. size (0.6 inch to 2 inches), is charged into the open top to a depth of about 16.4 feet after first putting a layer of coarse shale in the retort to cover the grid. Suitable kindling and some coke are then charged on top of the shale and ignited. By means of the exhauster, reduced pressure (subatmospheric pressure) is maintained in the retort, and the gases and vapors formed by combustion and pyrolysis are thus caused to pass down through the shale bed and out at the bottom of the retort. In this procedure a heat wave gradually passes down through the shale bed, whereby the shale oil and gases of pyrolysis are first expelled in the front portion of the wave, and the residue carbon is burned in the rear portion. It will be seen that in operating in this manner substantially all of the carbon residue in the shale would be burned if sufficient air were introduced, and the temperature finally attained would depend chiefly on the amount of such carbon remaining in the shale after the pyrolysis reactions had occurred. However, it was believed, in building these retorts, that with the shale available in the Balingen district the temperature in the bed would not rise to prohibitive heights; the moisture occurring naturally in the shale prevents the existence of excessively high temperatures in the zone of pyrolysis, i.e., in the front portion of the heat wave.

The "pull" by the exhausters is regulated so that the rate of travel of the heat wave down through the bed is approximately 20 cm. (7.9 inches) per hour. Under these conditions the negative pressure at the base of the generator will vary, it is said, from about -40 mm. at the beginning of the operation to about -80 mm. at the end, equivalent to -1.6 to -3.2 inches on a water manometer. These figures refer to pressure below 1 atmosphere and not to absolute pressures; they were estimated by the inventor for shale varying in size from 0 to 300 mm. (about 1 to 12 inches). Actually, in treating 0.6- to 2-inch shale at the specified rate, a greater negative pressure probably will be required.

No lining is provided in the Schweitzer retort because pilot tests indicated it was not necessary. The hot zone is not very thick, and the iron jacket (wall), being a good conductor, is expected to conduct and radiate heat from the hot zone at such a rate that overheating will not occur.

In the commercial-size unit, provision is made for removing the condensate that collects in the bottom of the retort separate from the vapors and gas, which are also removed from the bottom. Provision is made whereby

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the effluent gas stream will pass through coolers, condensers, and Cottrell electrostatic precipitators, and finally through an oil scrubber for removal of vapors of low-boiling liquid hydrocarbons.

After "distillation" is completed, the retort is to be lifted off its base by a traveling crane and removed to the residue receiving room, where it will be inverted and the spent shale dumped into a hopper connected to a crusher for breaking the residue lumps. A conveyor system is provided to take the crushed residue to a dump pile.

It is anticipated that most of the oil will collect in the Cottrell precipitators, from which it will flow through a water-oil separator steam-heated to 60° to 70° C., from which the oil will discharge into settlers. It was expected that the oil and water would separate and there would be no trouble from formation of emulsion.

Based upon the pilot-plant experiments, the results anticipated in the operation of the full-size plant were as follows:

Anticipated Results and Operating Conditions

Number of retorts operating	28
Shale treated per day of 24 hours, metric tons (1,102 short tons)	1,000
Size of shale charged, percent:	
0 to 3 mm. (0 to about 1/8-inch)	8 to 10
3 to 300 mm. (about 1/8- to 12-inches)	90 to 92
Temperatures, °C.:	
In combustion zone	1,200
In "distillation" zone (zone of pyrolysis)	450
In a zone 60 cm. (23.6 inches) below the "distillation" zone	60
Rate of downward travel of the hot zone, inches per hour	7.9
Negative pressure below grids at base of generator, inches of water below atmospheric:	
At the beginning of processing	-1.6
At the end of "distillation" period	-3.2
Residue yield, spent shale, percent	80
Oil yield, percent of Fischer assay, including benzine from absorber	85 to 90
Gas production per short ton of shale treated, cu. ft.	14,300

Composition of gas (pilot-plant results)

	Percent by volume
CO_2	26.0
H_2S	1.2
Illuminants	.5
CO	6.2
O_2	.7
H_2	3.5
CH_4	1.2
N_2	60.7
	100.0

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Calculated heating value of the gas, high value at 60° F. and 30 inches Hg., saturated, B.t.u. per cu. ft. 59

Composition of the shale residue

	Percent by weight
SiO_2	37.60
Fe_2O_3	7.70
Al_2O_3	12.00
CaO	27.00
MgO	2.05
Sulfur (as SO_3)	3.30
CO_2	.50
Carbon	2.50
Miscellaneous undetermined (difference)	7.35
	100.00

Investment costs

The cost of construction given to the authors by the inventor follows:

Total capital investment for a 28-retort plant is 6,500,000 Reichsmarks, equivalent (at 40 cents equal to 1 mark) to $2,600,000. This is equal to $2,600 per metric ton of shale per day capacity, or to $2,360 per short ton of shale per day.

On the basis of 56 retorts, or a plant for treating 2,204 short tons of shale per day, the estimated costs are said to be 9,000,000 Reichsmarks, or $3,600,000, which is equivalent to $1.633 per short ton per day capacity for treating shale. It is known that prisoner labor was used in Germany to a considerable extent, and, therefore, one should not rely too much on the accuracy of these cost estimates.

Remarks

In many respects the Schweitzer retort is similar to the N. T. U. retort,[4/] but differs in that it is open to the atmosphere at the top, has a water seal at the bottom, and a grid or grate that is permanently attached to the generator in a fixed position. The N. T. U. retort discharges the spent shale from the bottom (the bottom portion of that retort is removable), has a closed top, is adapted for controlled recirculation of gases, and is usually lined with refractory material, whereas the Schweitzer retort is supposed to work satisfactorily without a lining. It would seem that if the one can be used unlined, the other could, also, for operating conditions are substantially the same. The results obtained in treating a given crushed shale in the Schweitzer retort should not differ appreciably from

4/ Gavin, M. J., and Desmond, J. S., Construction and Operation of the Bureau of Mines Experimental Oil-Shale Plant, 1925-1927: Bureau of Mines Bull. 315, 1930, pp. 63-77.

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those obtained with the N. T. U. retort, and it is probable that better temperature control can be obtained with the N. T. U. In either case, important factors bearing on the yield of oil and retort capacity include the range in size of the shale pieces treated, ash-softening temperature, and caking temperature. Dust and very fine shale should not be included in the retort charge; neither should large shale be used. The temperature in the mass should not rise above the ash-softening temperature. Provision could readily be made whereby a controlled amount of steam (a definite amount relative to the air drawn into the shale process) would be supplied to the retort, thus offering a means of regulating temperatures and preventing overheating of the shale residue in the retort.

Portland Cement Works at Dotternhausen

The Portlandzementwerk, Dotternhausen, near Balingen, Württemberg, has been in operation for a number of years. Work on this plant was initiated in 1938 for the production of Portland cement from oil shale. For various reasons the plant was not completed until 1941, and it did not initially include the shale-treating retorts that are now a part of it. These retorts were under construction in 1942 but were not put into operation until 1944. The daily capacity of this plant as operated in 1944 and early 1945 was:

	Metric tons	Short tons
Cement	330	330
Hydraulic lime (so-called)	100	110
Shale oil (maximum)	10	11

The installation for winning oil from the shale comprised a battery of eight Meier-Grolman retorts (sometimes called Otto retorts, because they were built by the firm of C. Otto, Bochum). These retorts had a rated capacity of 66 short tons throughput of shale daily per retort, but actually only 44 to 55 tons were processed per retort, and only some of the retorts were in operation at any one time in 1944 and in the first few months of 1945.

Description of the Plant

For limestone:
- A limestone mine (open-cut) with steam shovel.
- Hammer-mill breaker.
- Conveyors.
- Raw-material silo.

For shale and cement:
- Steam shovel for winning shale.
- Open-pit mine on the property.
- Breaker.
- Classifier (sieves).
- Storage for crushed shale.
- Mill for limestone and shale residue.
- Silo for the mixture.
- Mixing ball mill for cement.

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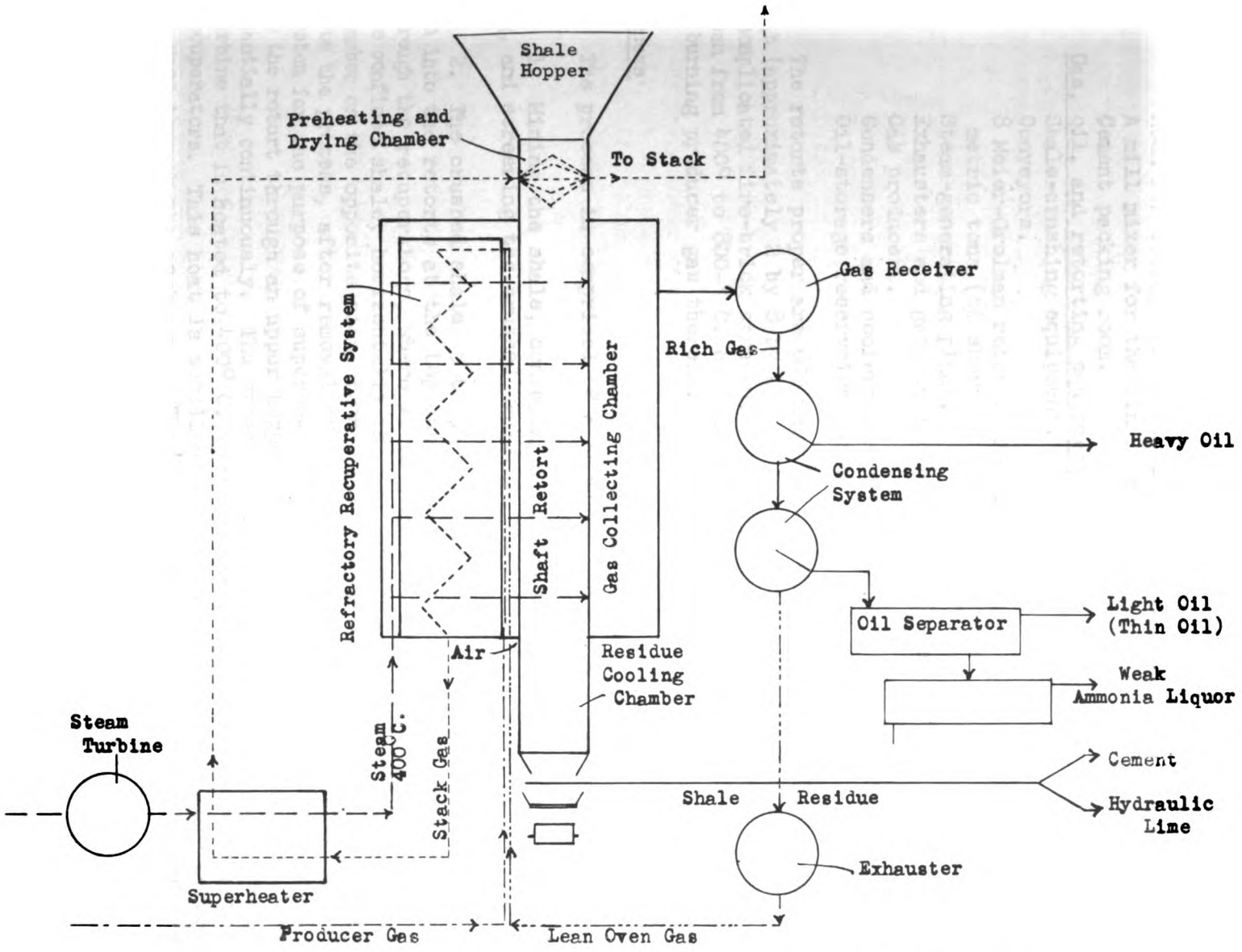

Fig. 2. - Diagram showing flow of fluids in the operation of the Meier-Grölman retort.

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Belt for sintering the cement mix.
Vibrating sieve that separates the treated, sintered material into portions according to size.
Room for storage of sintered materials.
A mill mixer for the final cement mixture.
Cement packing room.

Gas, oil, and retorting equipment:

Shale-crushing equipment.
Conveyors.
8 Meier-Grolman retorts, maximum rated capacity of each 60 metric tons (66 short tons) shale per day.
Steam-generating plant.
Exhausters and gas-pumping equipment (water pumps).
Gas producers.
Condensers and coolers and dry scrubber for recovering oil.
Oil-storage reservoirs, etc.

The retorts proper are 600 mm. wide, 2,400 mm. long, and 7,600 mm. high (approximately 2 by 8 by 25 feet). Each retort is built as a part of a complicated fire-brick structure with many flues that function to heat steam from 400° to 800+° C. by recuperative methods; the flues are heated by burning producer gas therein.

Process

The process is comprised of a number of separate steps, as follows:

1. Mining the shale, conveying it to crushers preparatory to retorting, and screening the crushed shale.

2. The crushed shale, 5 to 35 mm. size (3/16 to 1-3/8 inches), is fed into the retorts at the top until they are full. Then steam is passed through the recuperators, where it is heated to 800° C., and on through the confined shale, horizontally through louvres, into a gas-collecting chamber on the opposite side, from which gas and vapors are withdrawn. Gas from the process, after removal of the oil, is burned in the recuperative system for the purpose of superheating the steam. The shale is supplied to the retort through an upper hopper and is removed from the bottom substantially continuously. The steam supplied is the exhaust from a steam turbine that is heated to 400° C. in a heat exchanger before entering the recuperators. This heat is supplied by the stack gases, which are caused to pass through the exchanger. The stack gases leaving the exchanger pass through the upper portion of shale (incoming raw shale) supplied to the retort, heating it to about 200° C., thus drying it. Figure 2 is a diagram showing the flow of fluids in the operation of the Meier-Grolman retort.

3. The shale gas and oil vapors pass out of the retorts at the bottom, or rather, adjacent to the bottom thereof, and then through a cooling system, wherein the heavy vapors first condense and then, at a lower temperature, the hydrocarbons of lesser molecular weights are condensed and recovered separately from the heavy oil. The heavy product is called

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Dickol (thick oil) and the lighter or lower-density product is known as Dunol (thin oil). Of the total condensate, two-thirds are thin oil and one-third is thick oil or tar.

4. The spent shale is used with limestone in the production of Portland cement. Equal proportions of crushed shale residue and ground limestone are mixed with coke and a small amount of water, and the mixture is sintered on a slowly moving continuous-belt device (a Swight Lloyd Sinterband), on which the coke of the mixture is burned, raising the temperature of the mass to that necessary for sintering - 1,350° to 1,400° C. To this mixture an additional 10 to 15 percent of coke or coal and a small amount of water are added; the mixture is then conveyed to and over the sintering belt at such a speed that it is heated to 1,350° to 1,400° C. in half an hour. Suction is applied to the under side of the belt, and air is drawn through the mass, which is first ignited under an ignition hood. Combustion of the fuel in the mixture causes the sintering. The sintered material is stored for about 10 days and is then ground and admixed with finely ground shale residue for cement. Thus, 250 metric tons (275 short tons) of the sintered product are mixed with 20 to 30 percent of residue from shale, and this mixture is ground, yielding 300 to 325 metric tons (330 to 358 short tons) of cement per day. In the mixing of the residue (coke and water), pellets form, which are desirable feed stock for the Sinterband. Producer gas in the amount of 75,000 cubic feet per hour is used for starting combustion and initiating sintering of the pellets. An additional 34,000 cubic feet per hour of this gas is used at the mixing mill. (Mixing mill is shown at 12 in fig. 3.)

Shale Used

The full depth of shale (328 feet) is quarried immediately adjacent the plant, to which it is transported by rail. The shale passes first through a Krupp hammer-breaker, 90-horsepower, from which it is conveyed on a belt to a final crusher (Simon 65-horsepower). It then is screened, and the 3/16- to 1-3/8-inch sizes are delivered to bins that feed the shale retorts.

Composition of shale and shale products

Raw shale from Dotternhausen, oil-free basis (results as reported):

	Percent by weight
SiO_2	33.47
Fe_2O_3	6.18
Al_2O_3	9.50
$CaCO_3$	39.53
$MgCO_3$	2.81
SO_3	.20
S	3.19
	94.88
Water and undetermined (difference)	5.12
	100.00

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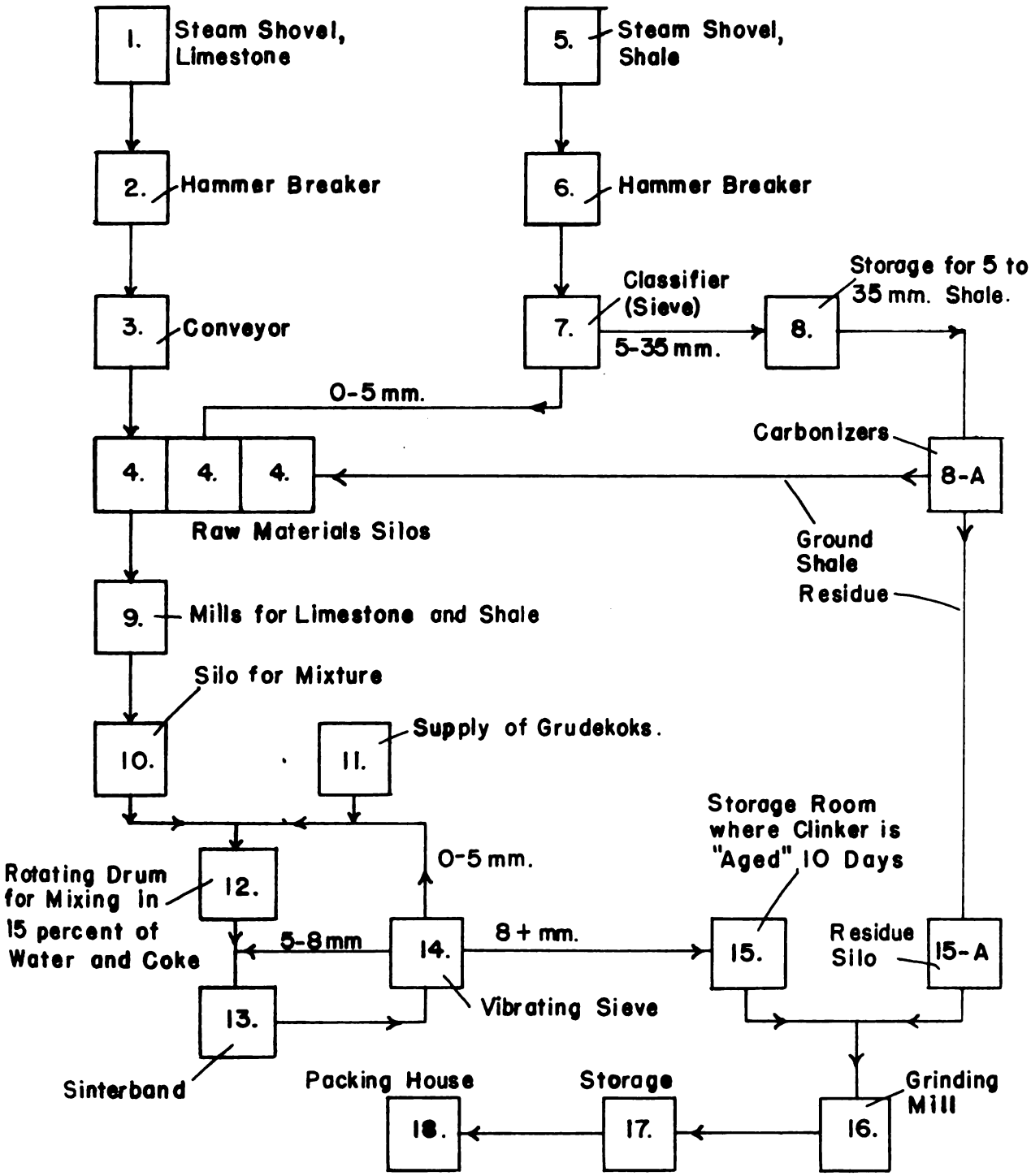

FIG. 3. DIAGRAMMATIC FLOW-CHART OF THE DOTTERNHAUSEN SHALE—TREATING AND CEMENT PLANT.

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A sample of residue from shale distillation, but obviously not from the above sample, gave the following results:

	Percent by weight
SiO_2	40.0
Fe_2O_3	6.8
Al_2O_3	14.6
CaO	29.0
MgO	2.0
Na_2O	2.2
SO_3	4.8
	99.4

The shale as mined commonly contains 4 to 5 percent H_2O and 4.5 percent of bitumen, of which latter 3.5 percent (percent of the shale) is recovered as total oil, equivalent to 70 pounds per short tons of shale, which amounts to approximately 8.8 U. S. gallons per short ton. Sample analyses of the shale oils showed the following:

Thick oil (heavy oil or tar)

	Oct. 31, 1944			Nov. 7, 1944
	Kg.	Pounds	Percent by wt.	Percent by wt.
Distillation:				
Light oil	2,130	4,695	14.4	16.67
Middle oil	4,275	9,422	29.02	24.73
Pitch residue	8,057	17,757	54.70	57.20
Lost	268	591	1.82	1.40
Total daily make	14,730	32,465	100.00	100.00
Specific gravity at 20° C			0.992	0.991
Flash point, °C			123	116
Viscosity (Engler) at 20° C			96.8	-
Viscosity (Engler) at 50° C			8.73	6.3

Thin oil

Engler distillation:

Temperature, °C.	158	200	250	300	330
Percent off by volume	Initial drop	7.0	31.0	59.0	71.0

Hard asphalt, percent by volume	0.48
Sulfur, percent by weight	4.10
Viscosity (Engler) at 20° C	2.18
Specific gravity at 20° C	0.92
Congealing point (pour point), °C	-21

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Composition of the gas evolved by retorting shale

	Percent by volume	
	Average	Range
CO_2	29.0	28.4-29.8
H_2S	3.5	3.4-3.6
Illuminants	.8	.7-.9
O_2	2.4	2.0-2.5
CO	2.0	1.8-2.3
H_2	16.4	15.6-17.4
CH_4	1.2	1.1-1.4
N_2	44.7	43.5-45.7
	100.0	

Calculated high heating value, dry gas at 0° C. and 760 mm. = 1,022 Kg.cal/m^3

Calculated high heating value, saturated gas at 60° F. and 30 in. Hg. = 107 B.t.u./cu.ft.

It is noted that this gas sometimes has a low heating value and can not be burned readily without preheating, preferably to a temperature of 200° C. or more. It is noted further that the gas contains 44.7 percent of N_2, which may be accounted for by the fact that air, producer gas, and stack gas are drawn into the retort.

Reported data for the production of shale oil during a particular day

Throughput per oven per 24 hours	46 metric tons (50.6 short tons).
Throughput per hour, total	9.61 metric tons (10.6 short tons).
Throughput per 24 hours, total	230.60 metric tons
Throughput per 24 hours, total	254.12 short tons
Steam to retorts, kg. per kg. shale (pound per pound)	0.68 to 0.77
Steam to retorts, kg. per metric ton of shale	680 to 770
Steam to retorts, pounds per short ton of shale	1,360 to 1,540
Gas made, Nm^3 per hour	2,734
Gas made, cubic feet[a] per hour	103,400
Gas made, Nm^3 per hour per metric ton of shale	284
Gas made, cubic feet[a] per short ton of shale	9,764
Low heating value of gas, kg.cal./Nm^3	957
Low heating value of gas, kg.cal./kg. shale	272
Low heating value of gas, B.t.u. per pound of shale	490
Generator gas used (producer gas), Nm^3 per hour	681
Generator gas used[a] (producer gas), cubic feet per hour	25,800
(For the heating of idle ovens, there is used 120 Nm^3/hr. included here, or 4,540 cubic feet.[a])	
Low calorific value of producer gas, kg. cal./Nm^3	1,082
Low calorific value of producer gas, B.t.u.[a]	113
Producer gas added, kg.cal./kg. of shale	50
Producer gas added, B.t.u. per pound of shale	90
Underfiring or retorts, kg.cal./kg. of shale, including about 100 kg.cal./kg. of shale through gasification with O_2 (air) in the retort	323
or B.t.u. per pound	581

a/ 60° F., 30 inches Hg., saturated with water.

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Mean temperature in the retort flues, in operation, °C..... 1,129

Temperature of gas leaving flues, °C..... 240 to 250

Shale gas composition:

	Percent by volume
CO_2	28.7
H_2S	3.4
Illuminants	.7
O_2	2.5
CO	2.3
H_2	16.4
CH_4	1.4
N_2	44.6
	100.0

Tar in shale (Fischer assay), percent..... 4.43

Total throughput, January 1 to June 30, 1944:

Metric tons of shale	38,884
Short tons of shale	42,850

Total tar (total oils) recovered, percent of the shale..... 3.47

Total tar (total oils) recovered, percent of Fischer assay..... 78.4

The yield of shale residue is approximately 80 percent of the weight of the initially mined shale.

It was stated that the retorting plant required 20 men per shift, or 60 men per day. This does not include the other labor necessary to plant operation.

The major items of the foregoing results, presented somewhat summarily but only in units standard in the United States, per short tons of shale, are as follows:

Shale used, 1 U. S. short ton (retorted) pounds	2,000
Producer gas used (113 B.t.u. per cubic foot, saturated at 60° F. and 30 inches Hg.), cubic feet	2,436
Steam to retorts (this is generated at 32 atmospheres pressure), pounds	1,360-1,540
Shale residue, pounds	1,600
Oil recovered (69.4 pounds), U. S. gallons	8.83
Shale gas produced,[a] cubic feet	9,764
Calculated heating value of shale gas,[a] B.t.u./cu.ft.	109
The total oil comprised:	
Heavy oil, one-third percent asphalt	54.0
Light oil, two-thirds, percent asphalt	1.0
The mean specific gravity of the total oil was	0.944
which is equivalent to pounds per gallon	7.836

[a] 60° F., 30 inches Hg., saturated with water.

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Because of the lack of cooling water and the high sulfur content of the shale gas, no attempt was made to recover the motor spirits left in the gas, which amounted to 5.[illegible] pounds per short ton of shale.

All of the shale gas made was used in firing the retorts. It is stated that when all of the retorts are in full operation there is enough shale gas to operate them, but when some of the retorts are idle and it is necessary to hold the idle retorts at an elevated temperature, extra gas (producer gas) is used. The producer gas was obtained from coke.

Although the retorts are said to have a rated capacity of 66 short tons per day, only 44 to 55 tons were put through each retort daily.

Figure 3 shows diagrammatically the flow of materials through the plant. Because sizing was considered important in the various operations, the different sizes are presented in the figure in the metric units actually employed, although approximate equivalents in U. S. standard units are given in the text. The operations (referring to fig. 3) are as follows:

The shale mined on the premises by steam-shovel methods is conducted directly to the hammer-mill breaker, 6, where it is crushed; it passes then to a screen classifier, 7, in which the 0 to 5 mm. (0- to 3/16-inch) shale is separated from the 5 to 35 mm. (3/16- to 1-3/8 inch) size. The latter is conveyed to a storage reservoir, 8, from which it is fed into carbonizer 8-A. The finer shale (0- to 3/16-inch) passes from classifier 7 to raw-materials silos 4. Limestone, separately mined, is similarly crushed in breaker 2 and is conveyed by conveyor 3 to reservoir 4. Equal weights of the shale residue and crushed limestone are conveyed to mill 9 with the fine shale from 7. The milled product from 9 passes to a storage reservoir, 10, for the finely ground mixture. The mixture from 10 is conveyed to mixer 12, wherein 15 percent water is added and 10 to 15 percent of Steinkohlekoksgrus (small-size coke) also is added, the mixture forming pellets or granules, which are led to Sinterband 13, where combustion of the carbonaceous matter occurs at such a rate that the mass is heated to 1,350° to 1,400° C. in the course of 30 minutes, the duration of its travel on the band. The speed of travel of the Sinterband is 1 meter (39.4 inches) per hour. Producer gas is used to ignite and initiate combustion of the carbonaceous matter. Suction applied to the under side of the band causes air to travel through the bed of granules at a desired rate, the depth of material being about 8 to 10 inches. The product from the Sinterband is divided into three portions by means of vibrating sieve 14. The portion 0 to 5 mm. (0 to 3/16 inch) in size is returned to the ball mill, 12, to be mixed into the granule mixture; the portion 5 to 8 mm. (3/16 to 5/16 inch) in size is added to the mixture conveyed to the Sinterband, whereas the remainder, 8 mm. (5/16 inch) and larger, is conducted to the clinker storage bin, 15, where it is aged 8 to 10 days. After the aging, the clinker is conveyed from 15 to 16, where it is mixed with an additional amount of shale residue from 15-A, and the mixture is ground to such fineness that 90 to 92 percent passes a 180-mesh sieve. The capacity is 18 to 20 tons per hour; the mixture thus ground comprises 70 to 80 percent of aged clinker and 30 to 20 percent of shale-residue. From mill 16 the

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cement is conveyed to packing house 18, where it is packaged; the capacity of the packing machine is 600 sacks per hour. A reservoir, 17, is provided for the ground cement.

When the cement plant is operated as described, the cost of producing cement is said to be 16.70 Reichsmarks per ton; this is an average for 1 year. With a 40-cent mark, the average is $6.06 per short ton of cement. The foregoing operating data and costs were given to the authors by responsible engineers at the plant. However, it is known that 500 slave workers were employed at this plant in addition to regular personnel, although operating labor is said to have been distributed as follows:

	Men
For operating carbonizing plant, (20 per shift)..	60
For operating remainder of plant.....	270
Total for whole plant and mine per day.....	330

The actual mining operation in the open-cut mine is said to require 7 men per shift or 21 men per day.

The fuel and power requirements of the cement plant only are as follows:

Total power per metric ton of cement is 95 kw.-hrs., including packing, this is equivalent to 86.2 kw.-hrs. per short ton of cement produced.

Fuel used to produce 357.5 short tons of cement per day is 55 short tons of coke of 9,360 B.t.u./lb. and 16.5 short tons of large Grudekoks (braunkohle char). Per short ton of cement, the quantities of fuel consumed are 308.0 pounds of coke and 92.4 pounds of large Grudekoks.

Strangely enough, no strength tests (briquet-breaking tests) were available, and apparently few, if any, were made. The cement was definitely satisfactory for use in constructing autobahn roads in Germany and for general building purposes; it is said to have the same tensile strength as good Portland cement. The authors of this paper believe that although the cement thus made is a useful product, proper allowance must be made, in preparing concrete mixtures, for the inert material initially present in the cement.

Hydraulic lime

The ground-shale residue is itself used as hydraulic lime. The lime content of the shale can be varied over an appreciable range because there are a number of 6- to 8-inch seams of limestone in the shale deposit. Although not stated in the interviews, it seems probable that high-lime shale is selected when hydraulic lime is made. The lime thus made is said to be excellent for plaster and agricultural uses. Because of the chemical composition, more of such lime would be required, when used for agricultural purposes, than a good-quality burned lime.

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The capacity for making hydraulic lime is, of course, the output of shale residue, but if the residue were all used as lime there would be no cement. Clearly it is not economical to sell hydraulic lime unless there is an excess of cement on hand or unless all of the 8 Meier-Grolman ovens are used for the pyrolysis of shale.

The cost of producing hydraulic lime is said to be 10 Reichsmarks per metric ton, or $3.63 per short ton, on the basis 40 cents equal one mark.

Power required for making hydraulic lime is 31.7 kw.-hr. per short ton.

Value of Liquid Fuel Recovered and Costs

A fixed price has been established by the Reich whereby a central bureau pays $80 (200 marks) per short ton for oil. However, when oil is sold directly to the farmer, who uses it in Bulldog tractors, the price is $112.40. At $80 per short ton of oil, the maximum credit used in computing returns is:

$\frac{\$80 \times 3.47}{100} = \$2.78$ per short ton of shale treated, the oil yield being 3.47 percent.

It is reported that when four or five Meier-Grolman retorts are operated, 231 short tons of oil is produced per month at a cost of $114 per ton. At this rate, approximately 5,600 short tons of residue useful in making cement is produced monthly. However, when 7 ovens are operated continuously, 363 short tons of oil and 8,800 tons of shale residue for use in making cement are produced monthly. The amount of electric current used per short ton of oil produced on this basis is said to be 590 kw.-hr.

Comments

Although the Meier-Grolman retorts were designed for distilling shale with superheated steam, it appears that the capacity was low when steam alone was used and that some internal combustion was practiced. The gas contains roughly 45 percent of nitrogen, which shows that for every 1,000 cubic feet of gas made 569 cubic feet of air or an equivalent high-nitrogen gas, such as producer or stack gas, was introduced into the retort. The yield of shale gas being 9,764 cubic feet per short ton of shale treated, the air or equivalent high-nitrogen gas supplied to the retorts was 9,764 x 0.569 = 5,555 cubic feet per short ton of shale treated (this air was for internal combustion and not for heating the flues).5/

With 7 of the 8 Meier-Grolman retorts operating at 55 short tons per day each, gas-handling, condensing, and cooling equipment must be supplied

5/ Obviously, recirculation of stack gas, producer gas, or mixtures of either or both with air would account for the nitrogen content of the shale gas. Under these circumstances the amount of air used would be that required to maintain the desired temperature in the shale in process.

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to care for 55 x 7 x 9,764 = 3,759,100 cubic feet of gas (at 60° F., 30 inches Hg., saturated) per day.

The matter of disposal of shale residue from retorting is generally recognized as an important problem in the treatment of most shales. This problem has been solved at this particular plant, but only so long as the production of oil is limited to that corresponding to the demand for cement and hydraulic lime.

The daily consumption of large Grudekoks for making producer gas was initially 132 short tons but has been reduced so that with four retorts operating it is 44 to 50 short tons daily, approximately equivalent to 385 pounds per short ton of shale treated. Thus, more fuel is used in the producer gas generator alone than is obtained as oil from the shale. For steam generation, 25 to 30 tons of coal is used daily, which is an additional charge of fuel consumed in the recovery of a small amount of oil.

Experimental Shale-Treating Furnace (Aluminum-Alloy Bath)

At this same location (Portlandzementwerk at Dotternhausen), the Company had erected and virtually completed an experimental installation of the pyrolysis of oil shale in a bath of molten aluminum alloy said to have a melting point of 580° C. Although this unit has never been operated, it was estimated by the Company that its rated capacity was 264 short tons of shale per day (half of the rated capacity of the whole main plant). The furnace comprised a rectangular, insulated, metal box containing about 50 tons of aluminum alloy. This box was divided into two portions separated by a baffle wall. One portion was in effect a Siemens Martin furnace, in which the alloy was heated by the direct firing of gas evolved in the process, the gas burners being placed near the top of the furnace; preheated air was to be supplied for burning the gas. Circulation of the molten alloy from the Siemens Martin section to the shale-treating section was achieved through the use of a paddle wheel.

The crushed shale, about 1/2 inch average size, is to be fed into the shale-treating section on a continuous belt. This belt, which is equipped with refractory paddles, will serve to cause the shale, as fed continuously into this chamber, to pass below the surface of the molten alloy. When these paddles lift out of the alloy bath at the end of their travel, the shale residue will float to the surface and be discharged at the end of the furnace and conveyed away. It was expected that the time of contact of the shale with the molten alloy would be about 5 to 10 minutes and that the reactions would be complete in that time. Provision was made whereby the gases and vapors evolved during pyrolysis would be removed by an exhauster as fast as they were generated. The shale oil was to be recovered by the usual recovery system, and the permanent gases were to be returned and used as fuel for maintaining the alloy bath at the selected temperature of 600° to 650° C.

While visiting this plant, the authors were informed that laboratory tests indicated that the loss of molten metal with the spent shale would

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be negligible. The tests yielded very little information to indicate that oil yield would be increased by this procedure, although calculations based upon laboratory experiments indicated that a very appreciable saving in labor would result from the use of the molten-bath process. It was stated that the gaseous atmosphere would be of a reducing nature in the section of the furnace where the hot gases would directly contact the alloy being heated. It was also stated that the alloy would not oxidize in this system. As aluminum oxidizes very readily, and as aluminum oxide is not readily reducible to the metal by reducing gas, the statement that oxidation will not occur cannot be accepted without verification.

The high capacity credited to this furnace is based upon laboratory experiments, which reveal that pyrolysis of small pieces of shale would be complete after a few minutes' immersion in a metal bath at a temperature of about 650° C. It was assumed that the permanent gases evolved in the process would not alone be sufficient to supply the necessary heat to maintain the alloy in a molten state, hence provision was made to supply the necesssry additional gas (producer gas). Upon leaving the furnace, the gaseous products of pyrolysis pass through a heat exchanger, which serves to preheat the air used for combustion of the gases which in turn are used to heat the alloy. A sample of the alloy was obtained for analysis.

The money needed to build this unit was furnished by the Reich.

Meiler Plants

(Deutsche Oelschiefer Forschung Gesellschaft, Schömberg, Württemberg (Near Balingen)

This Company was originally organized in 1943 by order of the Reich as a research organization to install pilot-plant shale-treating units and to determine from the operation of these units the most satisfactory and economical process for treating either Estonian or Württemberg shales. In July 1944, before experimental data of any importance were obtained, orders were given through the office of Reich Minister Speer for the immediate construction of 10 commercial Meiler-type plants, which were to be in operation by October 1944; these plants were to be supervised by the technical personnel from the pilot-plant station.

Commercial Meiler Plants

All of the 10 plants whose construction was ordered were not completed before the war ended in Germany. Their location and status in April 1945 were as follows:

No.	Location	Status
1	Nehren, near Tubingen	Completed and ready to start.
2	Bisingen	Operated for 3 weeks only.
3	Engstlatt	About 50 percent completed.
4	Erzingen (No.1)	Operated 3 weeks only.
5	Erzingen (No.2)	About 20 percent completed.

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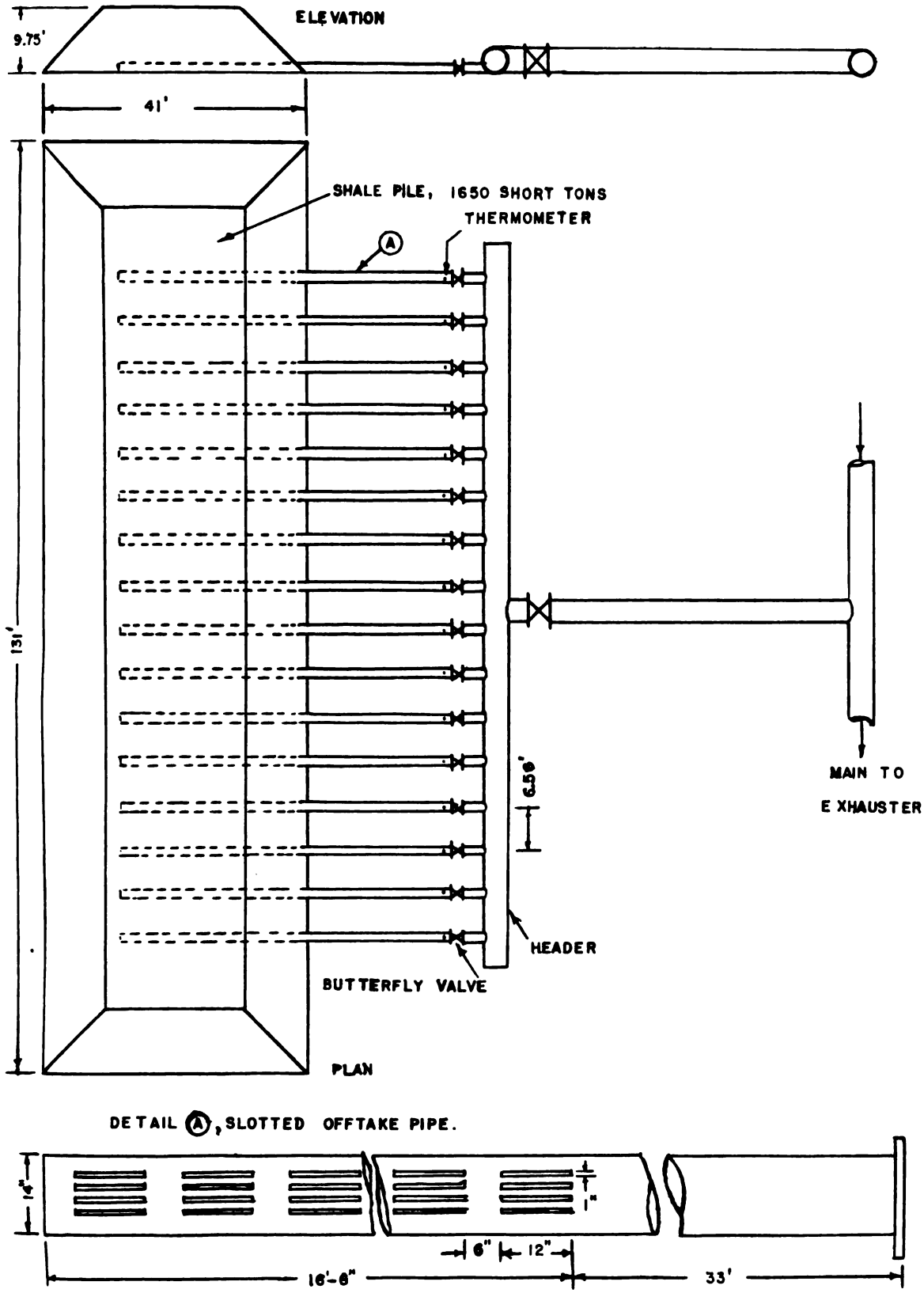

FIG. 4. MEILER SHALE PILE SHOWING PIPING SYSTEM.

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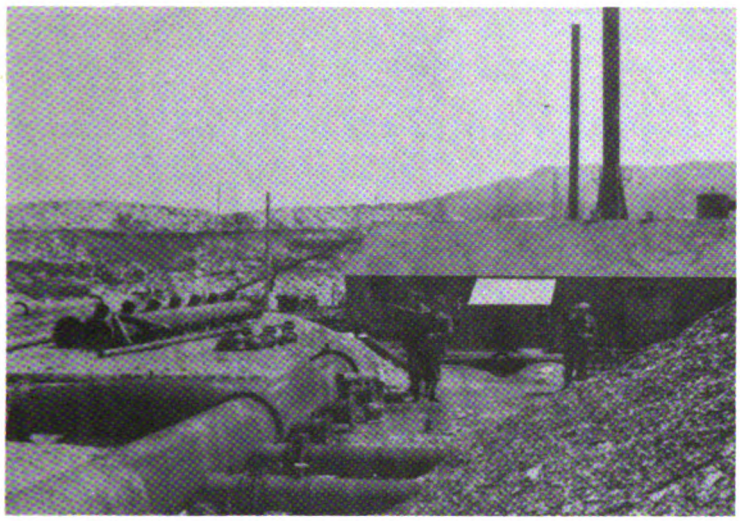

Figure 5. - Portion of a Meiler shale pile with header main and slotted offtake pipes in place.

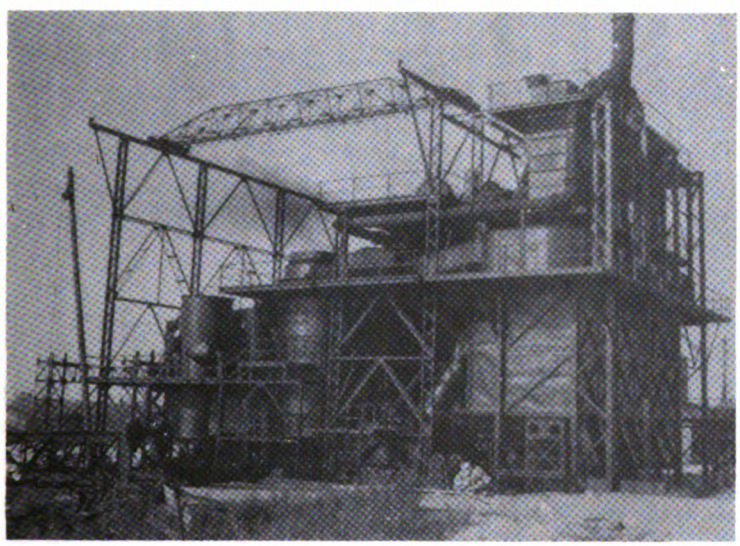

Figure 8. - New commercial unit at St. Hilair. Rated capacity, 550 short tons per day.

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No.	Location	Status
6	Dormettingen (No. 1)	About 30 percent completed.
7	Dormettingen (No. 2)	About 65 percent completed.
8	Dormettingen (No. 3)	Operated for 4 weeks only.
9	Schömberg	Operated for 3 weeks only.
10	Zepfenhan	About 60 percent completed.

The rated capacity of each plant for producing shale oil was 13,200 short tons of shale per month.

In the Meiler[6/] process, shale is treated much the same as wood was treated in the past for the production of wood charcoal, that is, piles of the crushed shale were so arranged over a series of perforated pipes connected to a manifold that when a fire was once kindled on the upper and exposed portion of the bed pyrolysis would take place at a predetermined rate by removing the gases formed through an exhauster connected in the system. In other words, air was drawn into the outer surface of a substantial pile of crushed shale at such a rate that a heat wave passed downward into the mass, the front of this wave being the "distillation" or pyrolysis zone and the back portion being a zone of combustion wherein the carbon residue in the shale was burned, furnishing the heat necessary for processing. Figure 4 is a sketch of the arrangement of the shale pile and the piping system through which the gases and vapors pass for the recovery of shale oil.

The Meiler field is a series, normally, of eight piles or beds of broken and crushed shale placed on top of a series of slotted pipes to a depth of 9.8 feet. Each pile is approximately 131 feet long and 41 feet wide. The total length and the number of beds employed depends on the terrain. Each pile contains approximately 1,650 short tons of shale. Each gas header main has 14 to 16 connections for pipes, which extend along the bottom of the bed as conduits for the products of pyrolysis. These pipes are placed 6-1/2 feet apart (center to center) and have a series of perforations or slots at one end on the top side; these slots are 20 mm. by 300 mm., or 0.8 inch wide by 11.8 inches long. Each header main, with its 14 to 16 connections, is joined to a main header in turn connected directly with the exhauster. Figure 5 is a photograph of a portion of a pile with the header main and slotted pipes connected thereto.

A valve is provided in each of these pipes, so that the gas drawn through them into the header main can be controlled. A thermometer extends into each of these pipes adjacent the valves, and the temperature of the gas passing through each valve controls the valve opening. Pipe sizes employed varied, and some of the headers and valves were said to be much larger than required owing to the necessity of using available materials. The slotted steel pipes had a diameter of 350 mm. (13.7 inches). Crushers ordered for these Meiler plants were not delivered, so it was

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6/ The word "Meiler" in this report has been used as descriptive of a system employing piles of shale. It should be noted that the word "Meiler" is German for stack or kiln.

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necessary to use weathered or readily broken shale of low oil content instead of the freshly mined crushed shale as was intended. It is necessary, of course, in such an operation to avoid the formation of flues or open channels through the bed of shale being processed, and this can best be done when the shale has a limited range of variation in size.

Operation

This system operates substantially as follows: A fire is started over the top of each of the 1,650-ton shale piles, and the exhauster is started to draw the products of combustion down into the bed and out through the piping system. Three or four hours are required to ignite the upper portion of the bed and heat it to the point of initial oil production. Approximately 2-1/2 days are required to "burn" the pile. The burning zone attains a temperature of approximately 1,200° C., whereas the pyrolysis zone is at a temperature approximating 450° C., and the gases with oil vapors leave the bed at about 60° C. The temperature of the offtake gas remains approximately 60° C. until the operation is about completed, at which time the temperature rises rather rapidly, finally reaching 250° C. at the end of the operation. When this temperature is reached, the bed is shut off from connection with the exhausters. The residue, commonly referred to as the ash pile, is 2-1/2 meters (8.2 feet) high; in other words, the bed sinks approximately 0.5 meter, or 1.64 feet, during processing. It was stated that when the available area had once been covered, new Meiler beds could be started on top of the old ones. It will be noted that the slotted tubes must be removed from the piles after pyrolysis is completed, and some little difficulty was experienced at the outset in accomplishing this.

Approximately 60 percent of the total oil recovered comes from the gas headers and is collected by a drainage system, whereas the other 40 percent is recovered largely from Cottrell precipitators. The oil as collected contains considerable water, and the mixture is settled in underground concrete storage tanks, where three layers commonly separate - that is, oil, emulsion, and water, the water being on the bottom and the oil on top. The practice is to pump the oil from the first settling tank through a heater, in which it is heated to 80° C., and again settle it in horizontal cylindrical tanks. Centrifuges were used to separate the oil from the emulsion, and the oil thus recovered contained less than 1 percent water.

One exhauster normally handles the gases from one Meiler field, but two may be required when a new bed is first fired. Each of these exhausters has a capacity of 1,062,000 cubic feet of gas per hour. The initial plan was to use at least some of the gas resulting from pyrolysis of the shale for generating steam by burning it under locomotive-type steam boilers. However, steam was generated by burning coal. Each exhauster was driven by a 200-kw. (268-horsepower) motor employing a gear box to control speed, which normally is 3,000 r.p.m. Suction equivalent to 60 mm. (2.36 inches) of water was maintained at the start of the operation in processing the shale; that is, the pressure was 2.36 inches of water less than atmospheric pressure. Subsequently the pressure decreased further, until at the end of pyrolysis it reached 80 mm. (3.1 inches) of water negative pressure.

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The gas recovered after removing the condensable matter had a very low calorific value and could be used with satisfaction only when it was preheated or special provision was made for its combustion.

Reported Result of Operation

The results said to have been obtained in the operation of Meiler fields are as follows:

Oil content of the shale	4.5 percent by weight
Oil recovery, percent of Fischer assay test	80+
Gas production per ton of shale (at 60° F., 30 inches Hg., saturated)	18,900 cubic feet
Total sulfur in the shale residue	2 percent
Composition of the shale oil:	
Specific gravity at 20° C	0.965
Sulfur content	3.0 percent by weight
Paraffin (wax)	2.0 percent by weight
Pour point	0° to 5° C.
Phenols	4.0 percent by weight
Water	1.0 percent by weight
Asphalt	0.7 percent by weight

The oil recovered was used as a Diesel fuel without further treatment.

The composition of the shale used is shown by the following analysis:

Composition (Free from Organic Matter)

	Percent by weight
SiO_2	35.0
Fe_2O_3	2.0
Al_2O_3	10.0
CaO	25.0
MgO	1.0
K_2O	3.0
CO_2	13.0
FeS_2	7.0
Water and undetermined	4.0
	100.0

Softening point of the ash (shale residue) 1,100° to 1,200° C.

Composition of Organic Matter (12 Percent of the Raw Shale)

	Percent by weight
C	81.4
H_2	8.8
N_2	1.7
S	.6
O_2	7.5
	100.0

Although organic matter is present in the shale in an amount approximating 12 percent, the total oil recoverable by the Fischer assay test is only 5.0 percent of the shale.

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Composition of the Gas from a Meiler Field

	Percent by volume
CO_2	20.0
CO	6.0
CH_4	1.0-2.0
H_2	1.0-2.0
O_2	5.0
H_2S	1.2
N_2	61.0-66.0

Calculated high heating value, B.t.u. per cubic foot (60° F., 30 inches Hg., saturated) 40-50

Benzine content of the gas at exit of Cottrell precipitators was 10 grams per cubic meter, equivalent to 10 pounds per short ton of shale. Although this benzine was not being recovered, it is included (above) in the stated yield of oil, being 80 to 85 percent of the Fischer assay test. The actual oil recovered, excluding this benzine, was 70 to 75 percent of the Fischer assay. Thus, with a yield of 5 percent total oil by Fischer assay, the recovery was:

Oil (recovered)...	70.0 to 75.1	pounds per short ton of shale or 70 to 75 percent of Fischer assay.
Benzine in gas.... (not recovered)	10.0	pounds per short ton of shale or 10 percent of Fischer assay.
Total.....	80.0 to 85.1	pounds, equal to 80 to 85 percent of Fischer assay yield.

Because of the lack of an ample supply of cooling water and the high sulfur content of the gas containing the benzine, no attempt was made to recover the benzine.

It was stated that with better sizing of the shale used in the Meiler fields, namely, employing 15 to 50 mm. (0.6 to 2.0 inches) pieces, the yield of oil would be 90 percent of the Fischer assay, and the oxygen content of the gas would be much lower than that shown in the above analysis. In that case the calorific value of the gas accordingly would be higher. The gas was said to have a calorific value of about 60 B.t.u. per cubic foot, but only one analysis (the one above) was supplied, and there was no evidence that additional tests had been made on large-scale operations.

Comments

Five of these commercial Meiler installations are ready to operate. Each of them is said to have cost 6,000,000 marks, which amounts to $2,400,000, considering the mark to have its old value of 40 cents. The oil produced was not refined or fractionated but was sold direct as fuel oil for Diesel engines and other purposes, and the prices were 282 marks ($112.80) per short ton to farmers and 200 marks ($80) per short ton to the Central (Government) Purchasing Bureau. It was stated that the

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over-all cost of producing the oil was 227 marks per short ton, which amounts to 36-1/2 cents per U. S. gallon.

The procedure followed in processing shale in Meiler fields is obviously simple, requiring a minimum of skilled labor and a type of equipment that can be supplied readily. It is believed that there was appreciable amount of corrosion in the pipe lines, but this can not be evaluated at this time.

Underground Pyrolysis of Shale

One company, known as Kohle-Oel-Union von Busse Kommanditgesselschaft, Schörzingen, Württemberg (near Balingen), operated a shale-treating plant underground more or less on an experimental basis, but on a sufficiently large scale to obtain data as to yields of oil and gas as well as information relating to the nature of the oil and some operating details. The idea of treating shale in this manner was based upon the Russian work on underground gasification of coal. Although this company was privately financed, it appears that the German Navy was much interested in the process for distilling shale and had entered into a 10-year contract with them whereby the Navy would provide 50 percent of the working costs and in return purchase the oil produced.

Preliminary experimental work on the process for treating shale underground was started at Holtzheim, near Stuttgart. The geological formation there was found to be unsuitable, the roofing being poor. Accordingly, work was discontinued and efforts were made along similar lines at Schörzingen about the middle of 1943. It apparently was the intention of the company to explore the field and work on the technical and practical problems involved in the underground pyrolysis of shale, believing that by avoiding the cost of mining all of the shale the process might prove to be economical. The plant at Schörzingen was therefore essentially a research or pilot plant until about the beginning of 1944. In December 1944, before the numerous problems had been solved, the company was obliged, under Government pressure, to commence operating on an enlarged scale for the commercial production of shale oil. Up to this time 16 experimental trials involving different operating methods and conditions had been made. The following is a description of the process in what is believed to be its latest stage of development:

The process comprises essentially the preparation underground of a series of chambers in which the shale, broken up by blasting, is ignited at one end of a tunnel of appreciable length and pyrolysis is promoted by exhausting the gases from the opposite end. In the larger-scale work recently carried out, two horizontal galleries 424 feet apart were prepared in the side of a hill at the level at which it was decided to work the shale. Cross galleries 197 feet apart were then provided to connect the two main galleries, and a "field" comprising two sets of 7 tunnel-like chambers was prepared by excavating the shale. Each of these tunnel-like chambers was 197 feet long, 6.6 feet wide, and 7.2 feet high. After preparing the chambers, the sides and roof were drilled to a depth of 4.9

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feet, and explosive charges were introduced therein. Upon firing the explosive charges, the remaining shale above and adjacent to these tunnel chambers was broken up, and the chambers were enlarged and filled with the broken shale. One end of each of the chambers was sealed off by double brick walls, into which an offtake pipe was extended for the withdrawal of products of pyrolysis. Wood and about 1 ton of coke were then charged into the opposite end of each chamber and ignited, and the chambers were then sealed off, except for an inlet opening for air at the end where the fuel charge was supplied. Air was drawn through the chambers by means of a motor-driven exhauster having a capacity of 530,000 cubic feet per hour, which was placed underground in one of the main galleries. The offtakes from each of these tunnels were connected to a common header, whereby one exhauster could handle the gases and vapors from the entire field. An auxiliary exhauster was provided on the surface and connected so that it could be used in case of a breakdown or failure of the underground exhauster. Figure 6 shows diagrammatically the arrangement of the tunnels and galleries in this plant.

The shale in situ was said to have a bulk density of 2.3 (143.5 pounds per cubic foot), but after being broken down by the explosive charges, which broke the shale into pieces up to about 1 foot in size, the bulk density was approximately 1.6 (99.8 pounds per cubic foot). It is therefore necessary to remove from its underground location an appreciable amount of the shale in order to treat the balance. In this particular instance it was found that 30 to 35 percent of the shale must be removed to treat the remainder by the procedure outlined herein. Moreover, the 30 to 35 percent that is removed must be satisfactorily treated above ground by an entirely different process before the whole procedure can be thought of as feasible. Calculations based upon the dimensions of the chambers quoted above show that a field of 14 chambers will contain approximately 26,400 short tons of shale as prepared for heat treatment.

After these chambers are sealed and the confined broken shale is ignited at one end of each chamber, pyrolysis is started by opening valves connecting the offtake pipes with the gas header main connected to the exhauster. The exhauster is so operated that pressure is maintained slightly below atmospheric in each of the chambers; the negative pressure varies along the length of these chambers from -2 mm. to -18 mm. (-3/32 to -3/4 inch of water). As a result of the steady evolution of gases and vapors from the shale, a zone of pyrolysis followed by a zone of combustion progresses slowly along the chambers toward the gas-outlet end. Although the rate of travel of the hot zone through the confined shale may be controlled by proper regulation of valves or exhauster-pull on the chambers, experience has indicated that the hot zone should progress at a rate of about 6 cm. (2.36 inches) per hour. At this rate, the time required for complete pyrolysis is approximately 42 days. It is said that if this rate is exceeded, the temperature will rise excessively locally; furthermore, the period of pyrolysis is so short that the larger lumps are not completely treated. The temperature of the gas at the offtake from the chambers usually remains at about 60° C. until the hot zone has progressed substantially from one end to the other in the chambers, that is, until the shale

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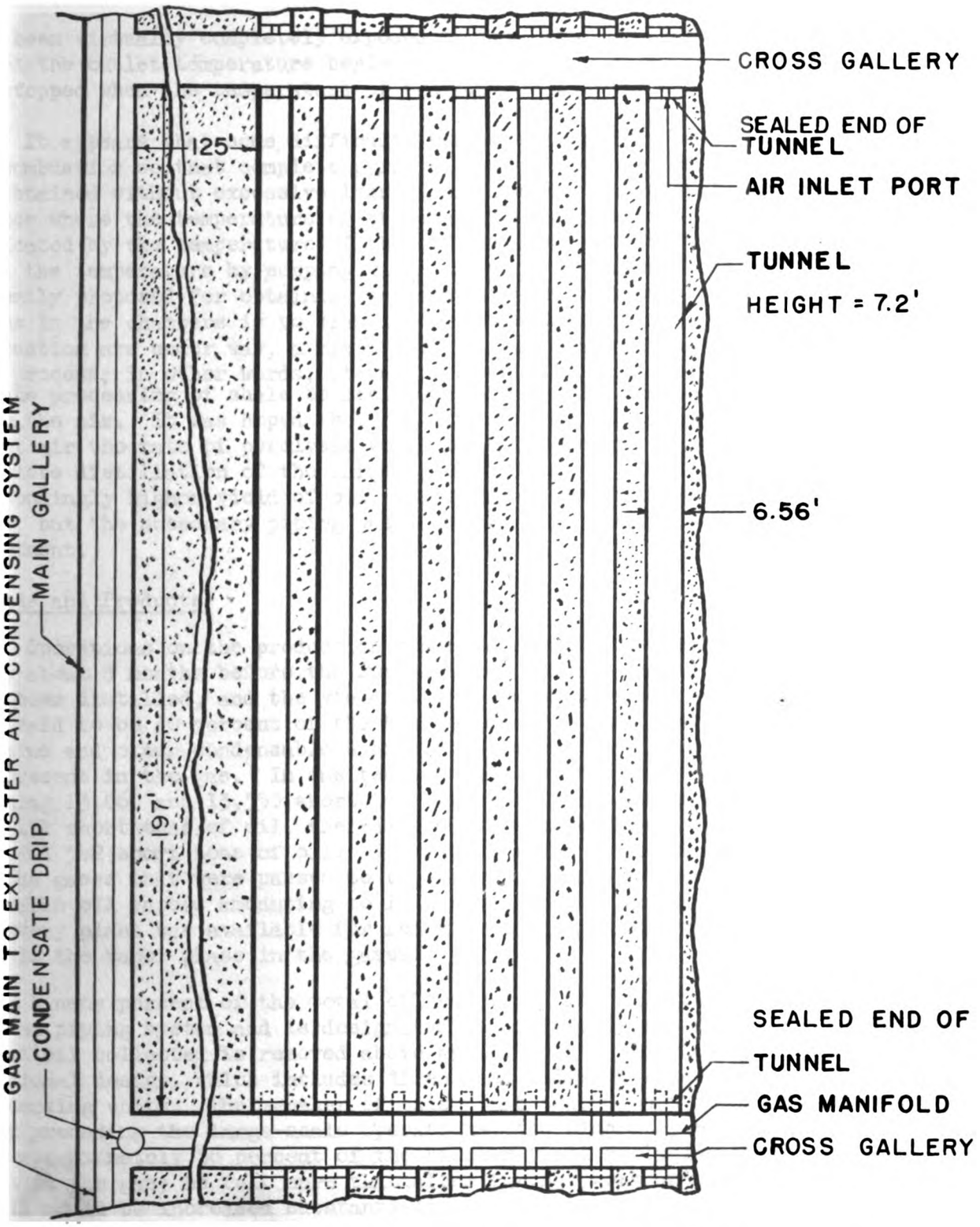

FIG. 6. DIAGRAM SHOWING ARRANGEMENT OF TUNNELS AND GALLERIES IN THE UNDERGROUND SHALE PLANT AT SCHÖRZINGEN.

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has been virtually completely exposed to the high temperature, at which point the outlet temperature begins to rise. The "pull" on the chambers is stopped when the temperature of the offtake gas is about 200° C.

It appears that some difficulty was experienced in regulating the rate of combustion so that complete pyrolysis of all of the crushed shale could be obtained without excessive loss of oil due to combustion. In one instance where the temperature of the shale in process rose excessively, as indicated by the temperature of the offtake gas, an effort was made to control the temperature by pumping water into the chambers. The method most recently proposed for obtaining satisfactory control over combustion conditions in the chambers is to draw into the chambers, while pyrolysis and combustion are under way, a mixture of air and some of the gases evolved in the process; in other words, it was proposed that some of the gases produced in the processing of shale be recirculated into the shale in process along with the air. It was hoped that by thus reducing the oxygen content of the inlet air the rate of pyrolysis would be under better control and that more complete distillation of the larger pieces of shale would result with correspondingly higher yield of oil. Experiments along these lines were not made, but the necessary piping was installed on chambers prepared for treatment.

Yields and Products

Operations on the production scale described above had been in progress only about 3 months before the European war ended. One field of 14 chambers had been distilled, and the yield of oil, based upon oil actually recovered, was said to be 30 percent of the Fischer assay. This yield does not include benzine and other condensable hydrocarbon vapors obtainable from and initially present in the gas. In one test, a field of two sets of 7 chambers containing 13,060 and 13,550 short tons of shale produced, respectively, 155 and 151 short tons of oil, whereas the respective Fischer assay yields were 522 and 542 short tons of oil. These yields did not include any light oil in the gases that were passed to the atmosphere and are said to contain condensable oil vapors amounting to 15 percent of the Fischer assay yield; no recovery plant was available for removing the light hydrocarbons that passed out in the vapor phase in the gases.

Ninety percent of the total oil recovered is collected from the underground piping system and is designated as heavy oil, and 10 percent of the total oil collected is removed above ground in a condensing system of conventional design, which includes direct and indirect water-scrubbing and condensing units. The manager of this plant stated that in the experimental work preceding the large-scale operations, the highest yield of oil obtained was approximately 56 percent of the Fischer yield exclusive of the light oil lost in the gas; he felt sure that after further work and experiment this yield could be increased substantially.

The light and heavy oils collected, respectively, above and below ground have properties, as indicated by the tests, as follows:

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	Heavy oil from underground	Light oil condensed above ground
Specific gravity at 20° C.	0.951	0.943
Water content, percent	0.98	0.47
Ash, percent	0.008	0.004
Congealing point	+1.0	-5.5
Flash point (open cup), °C.	104	95
Asphalt, percent	0.25	0.3
Conradson carbon, percent	2.64	2.04
Viscosity (Engler) at 20° C.	2.7	2.18
Viscosity (Engler) at 50° C.	1.52	1.39
Sulfur (total), percent	4.95	4.71
Corrosion, copper, (mg. per 16 sq. cm.)	45.8	47.5
Paraffin content (Butanol method), percent	3.28	2.15

Engler Distillation:

Temperature, °C.	140	200	250	300	350	390
Percent off by volume:						
Underground heavy oil	Initial drop	2.0	16.5	40.5	65.0 (congeals)	95.0
Oil condensed above ground	Initial drop	3.5	20.0	44.0	68.0 (congeals)	92.0

The volume and composition of the gas produced in this process vary appreciably with the volume of excess air employed. It was stated that the amount of gas made varied from 27,500 to 41,250 cubic feet[7] per short ton of shale treated.

A typical composition of the gas obtained is as follows:

	Percent by volume
$CO_2 + H_2S$	18.6
Illuminants	.5
O_2	2.5
CO	4.0
H_2	4.2
CH_4	1.5
N_2	68.7
	100.0

Benzine in the gas, grains/100 cubic feet[a] 155
Oil in the gas, grains/100 cubic feet[a] 213

a/ Gas measured at 60° F., 30 inches Hg., saturated.

Thus, if the gas yield is taken at 27,500 cubic feet per short ton of shale, the amount of benzine in the gas on the above basis would be 6.09

7/ Gas measured at 60° F., 30 inches of Hg., saturated.

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pounds per ton of shale; whereas, if the yield of gas is taken at the higher figure, viz., 41,250 cubic feet, the yield of benzine would accordingly be 9.13 pounds per short ton of shale. The oil in the gas measured on the above basis amounts to 8.36 pounds per short ton of shale, or to 12.56 pounds according as the gas yield is taken at the low or high value given above. As the higher figure for gas yield represents a condition in which a large excess of air is drawn into the shale in process, it seems only logical that the lower figures given for benzine and oil in the gas should be considered as the true benzine and oil content.

Size of Chambers

The above gas analysis shows that an appreciable amount of excess air was drawn into the system along with the gases evolved in the process and produced by combustion. It is obvious that air can readily pass over the top of the shale in the chambers unless the size of the chambers is regulated in accordance with the amount of explosive charges used for breaking down the roof and unless the depth of the holes drilled to receive the explosive charges also is regulated. In other words, it appears to be quite necessary that the chambers as prepared for pyrolysis be filled as completely as possible with the broken shale. Although the company had experimented with chambers 6.6 to 16.4 feet high, and obtained the best results from those 6.6 feet high, they planned to use chambers 5.2 feet high and 3.9 feet wide in subsequent experiments.

The amount of explosive material used per short ton of total shale treated was 1 pound.

Another important factor in arriving at a most satisfactory size for the preparation of tunnels is the thickness of the shale bed. It was noted that the shale deposits at Schörzingen were approximately 28.2 feet thick. These deposits contained bands of shale containing 3.4 to 7.5 percent oil according to Fischer assay tests.

Costs

The total capital invested in the plant at Schörzingen was said to be 2,400,000 Reichsmarks ($960,000), of which 750,000 Reichsmarks ($300,000) were invested in the plant and the remainder represented expenditures in research and development of the process.

OIL-SHALE INDUSTRY OF FRANCE

INTRODUCTION

This is a brief report of visits to oil-shale distillation plants in France made by the authors in June 1945. The French Government is striving to develop the known deposits of shale, particularly those in central and south-central France, for the purpose of supplying a portion of their requirements of motor fuel and lubricating oil, as the country does not have a natural ready source of supply of petroleum.

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The officers and other representatives of the companies whose plants were visited were most gracious and accorded every facility for obtaining information from their records and notes.

1. AUTUN

The first plant visited was that of the Société Minière des Schistes Bitumineux at Autun. It was found that this Company is operating 3 batteries of 40 retorts each of Pumpherston type. These retorts are exact duplicates of the well-known Scottish units in which shale is processed in Scotland. Crushed shale varying in size from 4 inches down to about 1/2 inch is treated continuously by passing it downward through the vertical retorts, which are externally heated by burning gases. The upper portion of each retort is made of metal (iron) and the lower portion, which is subjected to higher temperature, is made of refractory material. The capacity of each retort was initially 3.3 short tons of shale per day of 24 hours; this was at a time when superheated steam only was passed upward into the mass of shale in process, but later results, obtained when both air and steam were introduced adjacent to the bottom of the retort during processing, showed an increase to 7.7 short tons of shale per day per retort. The total maximum capacity with all retorts operating is 840 metric tons (924 short tons) of shale per 24 hours. The air is used internally to burn some of the carbon that otherwise would pass out as carbon in the spent shale; in this manner additional heat is generated for processing without the consumption of additional extraneous fuel. Although 350 cubic meters (12,350 cubic feet) of dry gas was generated from each metric ton of shale treated, more gas (producer gas separately generated) was required for heating the retorts. The amount of the producer gas used was the equivalent of 100 kg. of coal per 100 liters of crude oil recovered, or 3.33 pounds per U. S. gallon (the coal contained 30 percent ash); this is equivalent to 350 pounds of coal per barrel of 42 U. S. gallons of oil. It was said that 250,000 kg.-calories are required to distill 1 metric ton of shale (900,000 B.t.u. per short ton), whereas the gas obtained by the pyrolysis of shale with steam only produced 120,000 kg.-calories (433,000 B.t.u.). Air used during the processing of shale, generating heat within the retort by the combustion of residual carbon in the shale, supplies the required additional heat. The retorts were operated so that the temperature of the shale never rose above 1,000° C., because the shale softens at 1,100° C. and melts at a slightly higher temperature. The negative pressure at the top (offtakes) of the retorts is -66 mm. (-2.6 inches) of water. This reduced pressure is maintained by means of exhausters, of which there are three - two operating and one spare.

The chemical composition of the shale treated at Autun appears to differ somewhat from that of most American shales; at least, the oil obtained from heat-treating it is said to contain less wax. The oil characteristics are not reported here because they are published rather completely elsewhere. However, it is noted that the shale being treated yields 6 to 7 percent of total readily condensable oils by the Fischer assay retort, and that in plant operation the yield is 85 percent of Fischer yield. The shale contains 2.0 percent of total sulfur, of which 1.5 percent is pyrite and the remaining 0.5 percent is organic sulfur. The softening point of the shale is 1,100° C.

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Mining is by underground methods, the shale being 325 feet below the surface in a single seam 3.25 to 11 feet thick. Mining costs are high.

Five hundred men are employed in operating the mine and 400 in other operations. Thus, at full capacity of 924 short tons per day, the labor amounts to approximately 1 man-day per short ton of shale mined and treated.

It is noted that the usual condensing and cooling methods did not remove all of the oil, and that there was recovered, by oil-scrubbing the cooled gas, 7 to 8 liters (1.85 to 2.11 gallons) per cubic meter of shale, that is, per 1.2 metric tons of shale; this amounts to 1.4 to 1.6 U. S. gallons per short ton of shale treated. The total recovery of oil was 66 liters per metric ton, of which 6 liters were obtained by oil scrubbing. In U. S. units, the recovery was 15.8 U. S. gallons per short ton, of which 1.44 gallons were recovered by oil scrubbing. The crude oil has a specific gravity of 0.90.

Two oil scrubbers were used in series in recovering this additional oil from the gases. The oil used for scrubbing was the shale-oil fraction boiling in the range 240° to 260° C.

The shale used had a relatively low lime content, and there were no difficulties regarding residue disposal. A representative analysis of the spent shale is as follows:

	Percent by weight
SiO_2	51.52
TiO_2	.87
SO_3	1.92
Fe_2O_3	17.50
Al_2O_3	6.61
MnO	Trace
CaO	5.75
MgO	.50
K_2O	5.07
H_2O	.70
Loss on ignition, S, and undetermined	9.56
	100.00

A representative sample of crude oil obtained from the shale had the following characteristics, as revealed by the results of tests:

Specific gravity	0.895-0.905
Congealing (pour) point, °C	+5
Flash point (Luchaire), °C	+50
Viscosity (Engler), at 20° C	2.1-3.0
Viscosity (Engler), at 30° C	1.4-1.65
Conradson carbon residue, percent	1.1-1.9
Sulfur, less than, percent	0.5
Paraffin, percent	5 to 6
Hard asphalt, percent	0.3-0.5

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Engler distillation

Temperature, °C.....	174	195	213	245	273	297	320	344	370	381
Percent off by volume..	Initial drop	5	10	20	30	40	50	60	70	80

	Percent
Products removed by washing with 15 percent sulfuric acid.....	2.0
Products removed by washing with 20 percent caustic soda solution.	3.4

Ammonia is produced during pyrolysis and is recovered from the gas by washing with sulfuric acid. The total amount recovered, expressed as ammonium sulfate, is 10 to 11 kg. per metric ton of shale, which is equivalent to 20 to 22 pounds per short ton of shale.

The total electric power required for the operation of this plant was 60 kw.-hr. per 100 liters of oil produced, including the power required for mining and other purposes; this amounts to approximately 36.3 kw.-hr. per short ton of shale treated.

Water from the mine amounting to 10 tons per short ton of shale treated is used for condensing the oil and cooling the gas; this is just enough for the plant when the refinery is not in operation.

Because methods of treating oil shale have improved so greatly, the Company has decided to replace its Pumpherston-type retorts, as fast as they wear out, with Lantz retorts, which appear to offer substantial economies and greater earnings. The new retort was developed at St. Hilaire.

2. ST. HILAIRE

The next plant visited was that of the Société Chimique de la Grande Paroisse at St. Hilaire (Allier), France, where a pilot plant treating 88 to 100 short tons of shale daily has been in operation since 1938.

The Société was formed about 26 years ago for the purpose of developing the Claude process of making ammonia, but subsequently devoted attention to the production of synthetic motor fuels by high-pressure hydrogenation. These endeavors led to developments in the winning of oil from shale. After study of known processes, a distinctive retort was developed, known as the G. P. or Lantz retort. Certain major principles were kept in mind in conducting the experiments, namely:

(a) Indirect heating of the shale involves either mechanical intricacy or a low rate of production.

(b) Direct heating of the shale with gases of combustion or inert gases promotes dilution of the products of distillation, with its well-known consequences - a large condensing and oil-scrubbing plant is required and low light-spirit recovery results.

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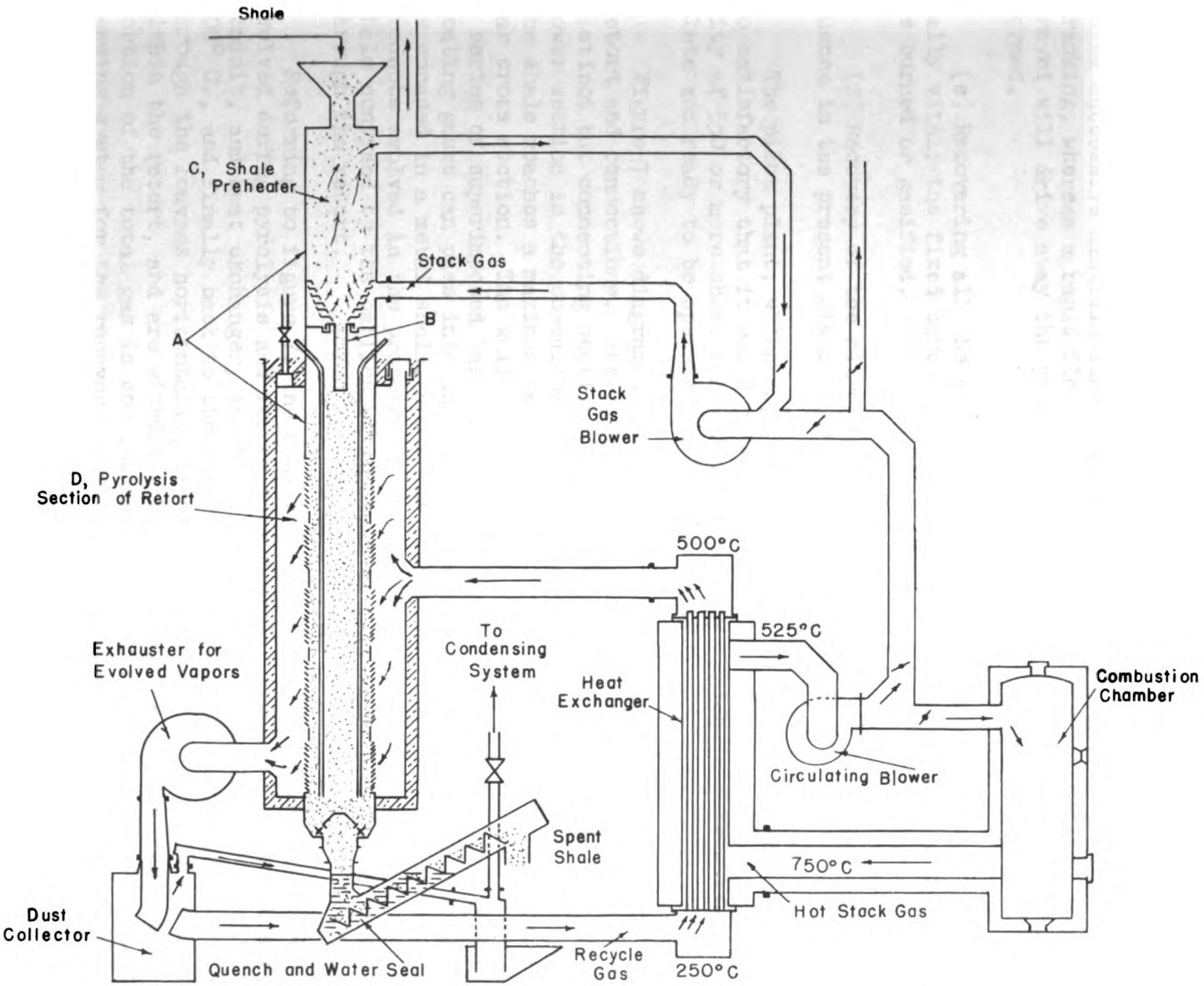

FIG. 7. DIAGRAMMATIC SECTIONAL VIEW OF THE LANTZ RETORT OF THE GRANDE PAROISSE, WITH GAS CIRCULATING SYSTEMS.

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(c) If one resorts to heating oil shale by direct contact with recycled gas, the cooling of the rich gas to ordinary temperatures for the purpose of removing condensable hydrocarbons entails high heat losses, because the water-vapor content is high and because the uncondensable gas thus cooled must be reheated to distillation temperatures before it is recycled.

(d) Circulating the gas in the retort countercurrent to the shale promotes successive distillations and condensations of the oil with subsequent cracking, whereas a rapid flow of gas at right angles to the line of shale travel will drive away the products of distillation as soon as they are formed.

(e) Recovering all the available heat content of the shale is economically vital; the fixed carbon left in the shale after evolution of oil must be burned or gasified.

(f) Recovery of the nitrogen as ammonium sulfate is of little consequence in the present state of the nitrogen industry.

The pilot plant, which employs a unique retort, gave results that were so satisfactory that it was decided to build a large unit with a rated capacity of 550 or more short tons of shale per day, which is substantially complete and ready to be operated at St. Hilaire.

Figure 7 shows diagrammatically a vertical section of the experimental retort and connections. The retort, which is vertical, is comprised of two distinct but connecting sections, each traversable by a gas stream. The lower section is the so-called "distillation" portion of the retort, wherein the shale reaches a maximum temperature during pyrolysis; it has a rectangular cross section. The walls confining the shale in this portion comprise a series of superimposed baffles that function as louvres, through which heating gases can pass into and through the confined shale. This section is encased in a metal shell, and means are provided whereby hot gaseous products evolved in the process are caused to pass horizontally through the shale confined by the baffles while shale is passing continuously downward through the retort.

Referring to figure 7, the exhauster removes the vapors and gases evolved during pyrolysis and forces them serially through a dust catcher, conduit, and heat exchanger, in which latter they are preheated to 450° to 500° C., and finally back to the retort. The gases thus preheated travel through the louvres horizontally, transferring heat to the shale confined within the retort, and are withdrawn by the exhauster and recirculated. A portion of the total gas is continuously withdrawn and conducted to the condensing system for the recovery of oil and gasoline. During this operation the raw shale crushed to 0.5- to 2-inch size is fed from the charging hopper above into the shale preheater. Here the shale is heated to approximately 150° C. by circulating through it a portion of the stack gas discharged from the heat exchanger. The shale in the retort and preheater is continuously moving downwardly and finally, at the bottom the spent shale, is quenched by passing through a water seal and is discharged by means of a screw conveyor. Heat is supplied to the heat exchanger by burning gas in the

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combustion chamber and circulating the hot products of combustion by means of the circulating blower. The gas evolved in the process is not sufficient to supply the heat requirements of the combustion chamber, hence separately generated producer gas is employed along with the excess retort gas. It will be noted that the bottom or discharge conveyor section contains water, which quenches the spent shale and generates steam, which passes up into the retort and out with the retort gas through the exhauster. The spent shale discharged from the conveyor contains 10 to 12 percent by weight of carbon, which ignites in the air and burns in the residue pile in spite of the quenching treatment.

In this operation the temperature attained by the shale in processing is limited to the temperature of the gas supplied to the retort from the heat exchanger. No air is used to supply heat by internal combustion in the shale mass and therefore excessively high temperatures are not reached and caking of the shale pieces does not occur. Furthermore, there is no dilution of the stream containing the oil vapors, and a minimum volume of gas is treated for the recovery of condensable hydrocarbons.

The shale used in these tests had a calorific value of 3,420 B.t.u. per pound, and the spent shale had a calorific value of 1,710 B.t.u. The oil content of the shale, or, rather, the oil recoverable from the shale as indicated by the Fischer assay, is 6.8 percent by weight; substantially all of this is recovered in the processing described. The spent shale contains 1.2 percent of total sulfur, and much of this burns to sulfur dioxide in the residue dump. During the processing there is evolved 860 cubic feet of gas per short ton of shale, and the calorific value of this gas after removing the gasoline vapors therefrom, is 628 to 690 B.t.u. per cubic foot, measured at 60° F., 30 inches Hg., and saturated.

The composition of the shale free of carbonaceous combustible matter is substantially as follows:

Composition of dry shale (free from combustible matter)

	Percent by weight
SiO_2	45.7
Al_2O_3	21.3
Fe_2O_3	10.5
CaO	14.0
MgO	2.5
SO_3	3.0
K_2O, Na_2O, and undetermined	3.0
	100.0

The softening point of the shale residue is 950° to 1,000° C.

The general composition of the raw shale, with special reference to the oil and water evolved and the carbon in the residue, is as follows:

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	Percent by weight
Shale	100.0
Oil recovered	6.6
Water	3.2
Carbon and combustible not recovered as oil	11.5
Total recovered	21.3
Residue	78.7

An average composition of the gas free from gasoline and oil vapors is as follows:

Composition of gas

	Percent by volume
CO_2	8.5
H_2S	7.7
Illuminants	4.3
O_2	0.0
CO	1.4
H_2	22.0
CH_4	31.0
C_2H_6	13.0
N_2	11.6
	100.0

The air-gas ratios are so controlled in the fuel-air mixture supplied to the combustion chamber that the oxygen content of the stack gas is less than 1 percent.

The gas analysis shows a nitrogen content of 11.6 percent in the scrubbed gas, which indicates that some of the stack gas circulated through the shale preheater passes down into the pyrolysis section of the retort. Apparently, operations should be so conducted that the flow of gas should be into the pyrolysis section rather than from it up into the shale preheater, as each 1,000 cubic feet of gases withdrawn from the system convey as much as 17 gallons of oil. The gases that are withdrawn pass through conventional cooling and scrubbing equipment for the recovery of oil and naphtha. Of the total oil recovered, 94 percent is classed as crude oil and 6 percent (recovered by the oil-scrubbing operation) is naphtha.

These two products have substantially the following characteristics:

	Oil	Scrubber naphtha
Specific gravity	0.910	0.700
Carbon, percent	85.8	-
H_2	11.3	-
Iodine number	30	200
Initial boiling point, °C	95	29

875

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Engler distillation (A.S.T.M.)

Volume percent off	5	10	20	30	40	50	60	70	80	90	95	end point
Temperature, °C:												
Oil	144	173	217	256	294	327	360	-	-	-	-	-
	41	47	54	60	67	74	82	92	103	118	128	141

In this process the shale travels through the retort at such a rate that every particle remains in the retort 4 hours, although it is said that the bulk of the shale is exhausted of oil in about 30 minutes.

The fans used for pumping the hot gases have water-cooled bearings, and although special high-chrome and high-nickel steels are not used, the corrosive effect of the gases pumped is said to be negligible.

The producer gas used as fuel in the operation of the pilot plant was made from coke, 30 kg. (66 pounds) of which was used per metric ton of shale treated; this is equivalent to 60 pounds per short ton of shale. It is estimated that 60 pounds of coke for producer gas and 860 cubic feet of shale gas will be required in a 500-metric-ton-per-day plant (550-short-ton-per-day) per short ton of shale treated.

The estimated water requirements for a commercial unit are 70 U. S. gallons per short ton of shale treated; this is the estimated amount of make-up water required.

The estimated power requirements are as follows: From the mine, entirely through the plant, the total power required per ton of shale treated is 9 to 10 kw.-hr. The total installed power in the new 500-metric-ton-per-day (550-short-ton-per-day) plant is 335 kw.-hr. The steam consumption in this process is substantially nil, being 0.5 metric ton per hour or 48 pounds per short ton of shale treated. For emergency use and fire protection, a capacity of 2.0 metric tons (2.2 short tons) per hour is installed.

The company felt that the performance of the pilot plant was so satisfactory that it was warranted in building a unit of this size. The future plans of this company include expanding the capacity to 2,200 short tons of shale per day.

One feature of this general process that needs correcting is the use of extraneous fuel, coke converted into producer gas, whereas the spent shale as discharged from the retort contains approximately 12 percent of carbon, which burns in the residue dump pile. The company engineers, recognizing this deficiency, have developed a special burner for recovering heat energy from the spent shale before discharging it to the dump pile. In future developments and installations at the St. Hilaire plant, it is probable that this new improvement will be incorporated and the need for producer gas made from coke eliminated.

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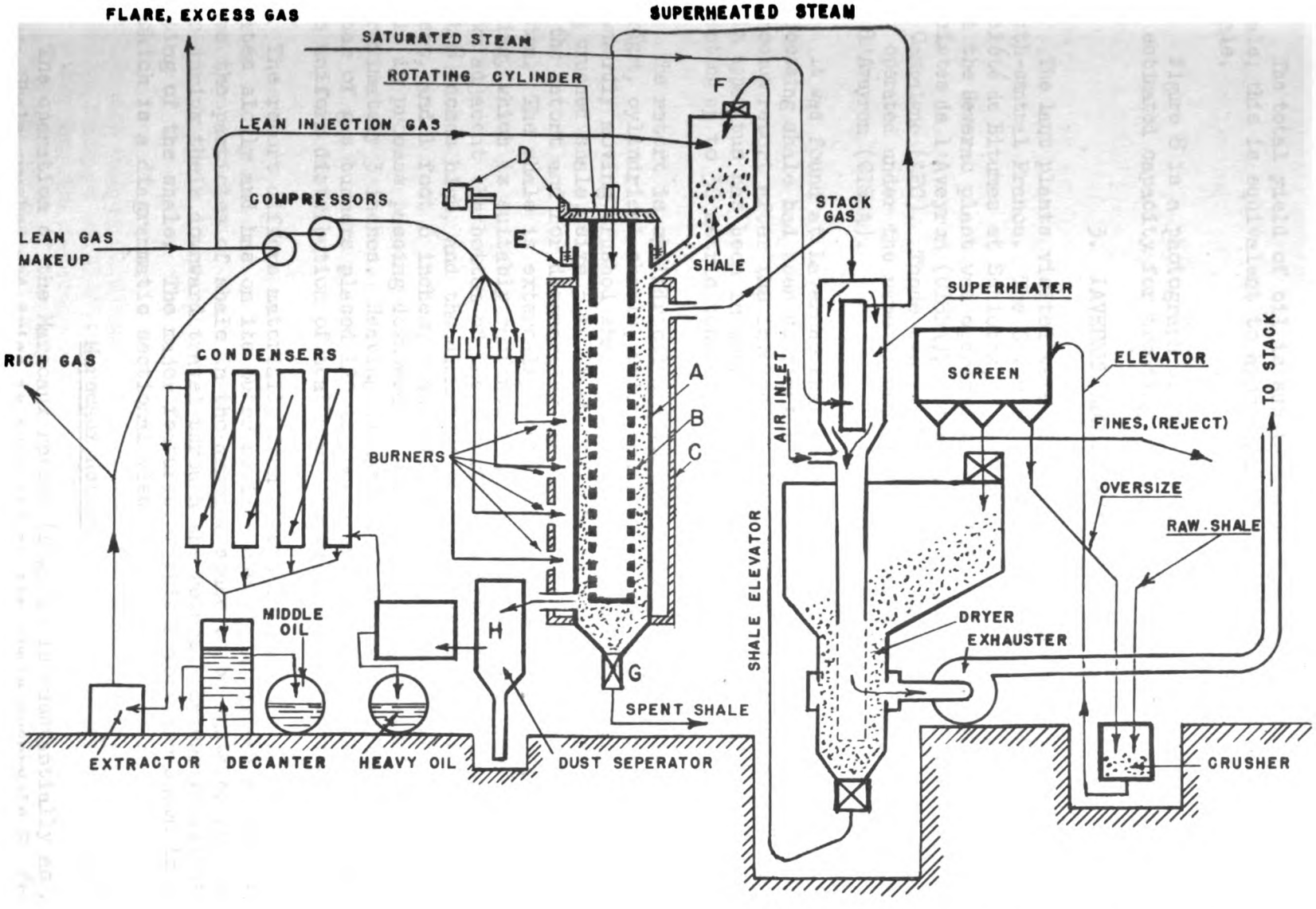

FIG. 9. A DIAGRAMMATIC SECTIONAL VIEW OF THE MARECAUX RETORT SHOWING THE PATH OF FLOW OF GAS AND STEAM.

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The total yield of oil is substantially 132 pounds per short ton of shale; this is equivalent to approximately 17.7 U. S. gallons per ton of shale.

Figure 8 is a photograph of the new unit installed at St. Hilaire with an estimated capacity for treating 550 short tons of shale per day.

3. LAVERNHE AND SEVERAC-LE-CHATEAU

The last plants visited were at Lavernhe and Severac-le-Chateau in south-central France. The Lavernhe plant was formerly operated by the Société de Bitumes et Schistes, a subsidiary of Lavernhe Monthand et Aulnoye, and the Severac plant was operated by the Compagnie Industrielle des Schistes de l'Aveyron (CISBA), a subsidiary of the Compagnie Alais Forges et Campaigne (AFC). These two parent companies have now merged and are being operated under the name of Compagnie Industrielle des Schistes Bitumineux de l'Aveyron (CISBA).

It was found at Lavernhe that an entirely different type of retort for processing shale had been substantially developed, which is known as the Marecaux retort after the inventor, who is a chemical engineer for CISBA. This apparatus has been in operation on a pilot scale for more than a year, treating up to 30 metric tons of shale per day.

The retort is cylindrical and vertical and comprises two concentric, upright, cylindrical shells, which confine between them a thin mass of downwardly moving crushed shale in process. Means are provided for charging crushed shale, size 3 to 25 mm. (1/8 to 1 inch), into the upper portion of the retort and for discharging the treated shale continuously at the bottom. The shale is externally heated through the outer cylindrical metal casing, which is suitably confined in a furnace, and the gases are withdrawn adjacent the bottom of the retort. The experimental retort is 19 feet 8 inches high, and the diameters of the outer and inner cylinders are 2 feet, and 1 foot 6 inches, respectively. Thus, the thickness of the shale in process passing downward between the two cylindrical surfaces is approximately 3 inches. Heating is applied to the outer cylinder by a number of gas burners placed 120 degrees apart and staggered vertically to give uniform distribution of heat over the wall of the outer cylinder.

The retort differs materially from others in that the inner cylinder rotates slowly and has on its outer surface cast-iron helical members that cause the particles of shale in the annular space to be agitated and turned over during their downward travel through the retort, thereby facilitating heating of the shale. The major features of this retort are shown in figure 9, which is a diagrammatic sectional view.

Marecaux Retort

The operation of the Marecaux retort (fig. 9) is substantially as follows: Shale crushed and dried is supplied to the shale reservoir F, from which it feeds into the retort proper, viz., into the space between cylinders

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A and B, as fast as the spent shale is removed at the bottom through offtake valve G. Heating gas is supplied through the burners to the furnace C, and the stack gases are removed at the top from the offtake. The stack gases are used for superheating the steam and drying the shale. The inner cylinder is suspended from the top on roller bearings and is rotated by virtue of motor and gears D. A water-seal, E, at the top prevents the escape of gases from the retort. Superheated steam is supplied through the top to the inner chamber of the retort. Openings in the inner cylinder wall are provided in such manner that the steam enters the shale in process at many levels. A series of pipes, which are a part of the rotating cylinder but confined on the inner side thereof, have a plurality of openings at different levels whereby the gases and vapors evolved are removed from the shale mass and conducted away therefrom, discharging at the bottom through the offtake to dust separator H. The superheated steam thus supplied not only aids in the pyrolysis of the shale, but it travels short distances through the shale in process and sweeps the gases and vapors as formed out of the shale mass into the offtake tubes. In this manner a product is obtained that apparently has not been cracked appreciably by over-exposure to heat. The total yield of oil from this method of treating shale, as obtained in tests of this retort, was 102 percent of the Fischer assay. Air was not introduced into the system, and therefore there was no internal combustion to liberate heat within the mass of shale in process. However, the steam used was superheated to a temperature of 400° C. All of the gas evolved from the shale was used, after condensing and removing the vapors therefrom, for heating the retort. Additional gas was required for this purpose, which was obtained from a separately operated gas producer.

The amount of gas evolved strictly by pyrolysis was 14 to 15 cubic meters (529 to 567 cubic feet) per metric ton of shale treated; this is equivalent to 481 to 515 cubic feet per short ton of shale. The gas and vapors evolved in the process pass from the retort through a dust separator and a heavy oil seal-pot containing oil at 118° C., and then to a condenser system, where middle oil and lighter oils condense and are separated from the fixed gases.

Although the total amount of oil produced, including gasoline, is said to be as high as 102 percent of the Fischer assay yield, this amount was not actually recovered; some of the gasoline and light condensable hydrocarbons known to be present in the gas were not removed therefrom, because this was only a pilot plant and the installation of equipment necessary for recovering these products was considered unnecessary. It is known that because of the high sulfur content of the gases evolved from the shale, unusual methods for recovering them from the light hydrocarbons will be required. The total amount of oil actually recovered from the shale treated in this retort, exclusive of the gasoline vapors left in the gas, was 41.83 kg. per metric ton, or 83.66 pounds per short ton of shale; this yield is equivalent to 92 percent of the Fischer assay.

The maximum temperature in the furnace was 700° C., whereas the maximum temperature of the outer retort shell, which is the heating surface of the retort, was 550° C. The temperature of the gaseous products of combustion leaving the furnace chamber at the top thereof was 450° C., whereas the maximum temperature reached by the shale in process was approximately 450° to 475° C.

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The total heating surface of this retort was 9 square meters (96.8 square feet); therefore, the amount of shale that could be treated per day amounted to 3.3 metric tons per square meter of heating surface, which is equivalent to 675 pounds per day per square foot of heating surface. The gases and vapors are removed from the retort under a pressure slightly below atmospheric, whereas the steam supplied to the shale through the inner cylindrical chamber is at a pressure somewhat above atmospheric.

The amount of steam used was 40 to 50 kg. per metric ton of shale, or 80 to 100 pounds per short ton of shale. The shale charged per day was 30 metric tons maximum, which is equivalent to 33 short tons per day. The shale charged was approximately 28 pounds per square foot of heating surface per hour. The rich gas made was 1,030 cubic feet per short ton of dry shale.

The actual heat energy supplied to the retort was said to be 260,000 kg.-calories per metric ton of shale; this is equivalent to 936,000 B.t.u. per short ton of shale. The steam used was produced from the water jacket of the gas producer. Inasmuch as the gas producer was oversize as compared to the retort, it is not clear whether enough steam will be produced in this manner in commercial installations. The producer gas was made from semicoke, but consideration has been given to the possibility of using the carbon residue in the spent shale as a source of heat for heating the retorts, and experiments will be conducted along this line when the larger units are employed. The amount of producer gas required may be approximately determined by difference, as follows, on the basis of 1 short ton of shale:

	B.t.u.
Total heat required	936,000
Heat of combustion of shale gas	249,000
Difference	687,000

As the heating value of the producer gas is 80.5 B.t.u. per cubic foot (high value, 60° F., 30 inches Hg., saturated), the amount of producer gas required, according to the foregoing, is 687,000 ÷ 80.5 = 8,523 cubic feet per short ton of shale. These figures are not in complete agreement with the results of a series of tests made in the experimental retort under the guidance and assistance of a French engineer reporting on this process. The results obtained in the course of the latter tests are as follows:

	Per short ton of dry shale treated
	Pounds
Products:	
Middle oil	68.26
Heavy oil, water and dust deducted	7.3
Other condensation products	1.6
Gasoline in the gas	7.4
	Cubic feet
Pyrolysis gas (at 60° F., 30 inches Hg., saturated)	515
Gas actually withdrawn from the retort containing some recirculated producer gas	1,134
Consumption of lean gas (producer gas plus fixed gases of pyrolysis):	
(a) To the retort burners	12,474
(b) For injection into the oven	605

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	Per short ton of dry shale treated Pounds
Material balance:	
Middle oil recovered	68.26
Heavy oil, water and dust deducted	7.8
Other condensed liquids	1.6
Total oil	77.66
Gasoline in the gas (density 0.681)	7.4
Total liquid products produced	85.06
(Total liquid products produced = 4.253 percent of the dry shale treated)	
Pyrolysis gas	32.72
Water of condensation	20.00
Shale residue	1,862.22
Grand total	2,000.00

Oil content, according to Fischer assay test = 4.2 percent

Characteristics of products consumed and recovered

Middle oil:

Middle oil (density at 20° C.)	0.930
Water content	Trace
Dust, percent	0.06
Acidity	Trace
Sulfur, percent	3.24
Phenols, percent	1.1
Viscosity centistokes:	
At 20° C.	10.2
At 35° C.	6.2
At 50° C.	4.7
At 100° C.	1.46

Fractional distillation:

First drop off at 108° C.
10 percent off at 160° C.
20 percent off at 205° C.
30 percent off at 252° C.

Balance of distillation conducted at 2 mm. Hg. absolute pressure:

40 percent off at 142° C.
50 percent off at 180° C.
60 percent off at 205° C.
70 percent off at 243° C.
80 percent off at 283° C.

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Heavy Oil:

Heavy oil (density at 20° C.)	1.023
Water content, percent	2.9
Dust, percent	2.0
Acidity	None
Sulfur, percent	2.98
Phenols, percent	0.76

Viscosity centistokes:

At 20° C.	2,200.0
At 35° C.	380.0
At 50° C.	111.0
At 100° C.	10.5

Distillation under vacuum

Fraction percent distilled	Temperature, ° C.	Absolute pressure, mm. Hg.	Density at 15° C.	Pourpoint ° C.
10	197	4	0.930	-18
20	223	4	0.967	-18
30	260	5	0.936	-18
40	280	7	1.002	-5
50	300	8	1.008	+17
60	326	10	1.011	+23
70	345	12	1.035	+29

Residue, percent	22.5
Loss and unaccounted for, percent	7.5

Composition of gases

Composition of lean gas:	Percent by volume
CO_2	9.5
CO	18.4
H_2	8.2
O_2	Traces
N_2 (by difference)	63.9
	100.0

Low heating value.....770 calories per cubic meter (80.5 B.t.u. per cubic foot at 60° F., 30 inches Hg., saturated):

Calculated composition of pyrolysis gas

	Percent by volume
H_2S	24.2
CO_2	21.6
CO	0.0
CH_4	9.2
H_2	20.2
C_2H_6	9.8
N_2 (by difference)	15.0
	100.0

873

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This is the composition of the gas after the removal and condensation of the higher hydrocarbons; and it has a value of 4,600 calories per cubic meter (481 B.t.u. per cubic foot, higher heating value at 60° F., 30 inches Hg., and saturated); it is stated that normally the true heating value of this gas is 4,500 to 5,000 calories per cubic meter (470 to 522 B.t.u. per cubic foot higher heating value at 60° F., 30 inches Hg., and saturated).

Total Heat Supplied to the Retort

The heat energy supplied to the retort is as follows:

	B.t.u.
(a) Lean gas to heat retort - 11,350 cubic feet per short ton of dry shale at 80.5 B.t.u. per cubic foot.....	914,000
(b) Injection (per short ton of dry shale):	
563 cubic feet of lean gas.....	45,400
66.9 pounds of steam at 100° C. (212° F.).....	76,000
Total B.t.u. per short ton of dry shale.....	1,035,400

It should be noted that the injected gas referred to above is that portion of the total lean gas that is introduced into the dry-shale reservoir for the purpose of preventing tar vapors from accumulating therein and which ultimately passes down into and through the mass of shale in process.

Although the Marecaux retort has not been tried on a large scale, it appears that sufficient data are at hand to permit computing the results that might be expected, with a larger unit, and there appears to be no reason why the smoothness of operation in the pilot plant should not also be experienced in a commercial installation. The company is so satisfied that this retort is economical and an improvement over retorts used in standard practice that two commercial units of 120 tons each are now under construction at their plant at Severac.

Since the merger of the two companies referred to above, plans have been formulated for a large-scale study of shale processing. It is proposed that there will ultimately be installed at Severac processing equipment capable of treating 3,000 tons of shale per day. At this plant there is now under construction one Petit furnace, one Lantz retort, and two Marecaux retorts. The Petit retort is being installed, it is said, chiefly because the material can be obtained at this time; no information was available that would lead one to believe that results thus far obtained in experimental operation of a small Petit retort were better, in general, than those that might be obtained with either the Lantz or Marecaux retorts.

Petit Retort

The Petit retort developed at Grenoble (by CISBA) on a pilot-plant scale only apparently has never been operated on a scale larger than 8 tons per day. At least, the authors do not have any information relating to a larger-scale

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operation. The process differs from others chiefly in the fact that the shale prior to distillation, is wetted with the shale oil from previous distillations, the oil-wetted shale subsequently passing through a horizontal, rotating, externally heated cylindrical retort comprising two concentric cylinders. The shale in process is caused to pass serially through the inner cylinder and back in the reverse direction through the space between the cylinders, discharging at the inlet end of the retort. (The pilot plant employed only a single, one-pass, cylindrical retort; the retort under construction, and on a larger scale has the double cylinders.) The object of the oil-wetting treatment is to cause solvent action and deploymerization of the kerogen. Owing to the fact that only a small portion of the retort heating surface is in contact with the shale in process, and because of the general nature of the methods employed for applying heat to this retort, it is doubtful whether it will be of interest in the treatment of American shales. The retort, being externally heated, is confined in a furnace, thus exposing a large outer surface for the radiation of heat. The information available to the authors of this paper relating to the performance of the Petit retort is too meager to warrant making positive statements regarding its performance and utility. More information will be obtained through the operation of the retort now being installed at Severac.

The authors wish to acknowledge the wholehearted cooperation of the directors and officers of the companies contacted and their engineers who were most cordial and helpful to them in obtaining the information relating to the development of an oil-shale industry in France.

REVIEW OF LITERATURE ON OVENS AND RETORTS FOR TREATING BITUMINOUS SHALES

While studying the developments in France in the production of shale oil, there was made available to the authors a report prepared rather recently by a French research association reviewing the various available processes and types of retorts as to their applicability and possible usefulness in the treatment of French shale. This report contains so much useful information relating to present practice and tendencies in this field that it has been translated and is presented below in lieu of a description based upon information obtained elsewhere relating to the same subject matter. The figures have been redrawn and are not exact copies from the report.

LITERATURE REVIEW BY
CENTRE D'ETUDES ET DE RECHERCHES
DES CARBURANTS ET LUBRIFIANTS DE REMPLACEMENT,
JUNE 1943.

Pyrogenation Ovens for Bituminous Shales

General Considerations

Bituminous shales consist of rocks containing a certain proportion of organic matter known as Kerogen, which furnishes a mineral oil by pyrolytic distillation.

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This oil does not exist as such in the shales. In fact, when shales are treated with the customary organic solvents, only traces of resinous products are obtained. Consequently, the oil is formed through the pyrolysis of the organic matter originally present substantially as the carbonization of coal forms tars that did not exist as such in the original matter subjected to the pyrolysis. This characteristic differentiates shales from impregnated limestones, the organic compounds of which distill without decomposition and which are soluble in solvents, which indicates that they existed as such in the rock.

The organic matter of shales has a hydrocarbon basis. It contains, besides carbon and hydrogen, some oxygen, nitrogen, and sulfur. It is possible to recover the nitrogen as ammonia, whereas sulfur is an interfering element, the elimination of which requires costly refining. However, attempts are being made to recover the sulfur from the hydrogen sulfide evolved during distillation.

Upon heating in enclosed vessels, shales yield combustible gases that carry a certain proportion of light benzine, crude oils, and, if the shale is heated to a high temperature at the end of the operation, ammoniacal water. There remains in the retort mineral matter and fixed carbon.

The distillation temperature is about 450° C., the oil being driven off between 430° and 480° C. The reaction is slightly exothermic. At 450° C. certain shales show a tendency to soften and to cake or agglomerate. It will be seen later that this characteristic greatly influences the type of apparatus to be used for the pyrolysis.

The residual mineral matter consists of complex silicates containing mostly alumina and ferric oxide. Their softening points vary, depending on the oil content of the original shale; for French shales it is seldom lower than 1,000° C.

These mineral residues retain fixed carbon in a very finely divided state and in a very reactive form. This carbon is readily combustible, and it can thus be utilized as a fuel when the carbon content is higher than about 6 percent.

If the pyrolysis of the shales is carried out in the presence of steam, distillation is more rapid and yields of oil are larger. Moreover, a good part of the nitrogen is changed into ammonia if the temperature is high enough. Shale oil differs from petroleum in that it contains a larger proportion of unsaturated hydrocarbons; it differs from the primary tar from either coal or lignite by its lower density and lower content of phenolic compounds.

Characteristics of Bituminous-Shale Ovens

Whereas the pyrolysis of coal and lignite produces solid, liquid, or gaseous compounds, all of which have salable values, the treatment of shales is complicated by the presence of an enormous proportion of worthless mineral matter, which has to be handled and the heat of which is a total loss. The existence of this worthless gangue determines the general characteristics that are common to the various types of shale ovens.

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(a) The cost and size of shale

The most important problem is to reduce the cost of handling the inert constituent; that is to say, reduce to a minimum the cost of the shale brought to the plant. This is a problem that affects subsequent pyrolysis only with regard to the size of the shale. It can be seen that for economical reasons crushing should not be carried out farther than is necessary for a good heat transfer; shale ovens should be able to handle medium sizes, the pyrolysis of the fines being limited in this industry to the amounts of fines unavoidably produced in the crushing operation.

(b) Apparatus

As dense and cheap material is being handled, carbonization must be carried out at the maximum rate without interruption, that is, shale ovens must be run continuously. Throughput also must be very large so as to spread exploitation costs and plant amortization over as large a daily production as possible. To diminish the original plant costs, upkeep, and chances of breakdown, simplicity of design is essential. Consequently, mechanical ovens, which require extra power, are generally given secondary consideration. In fact, mechanical ovens are used only for treating fines or shales having a low softening temperature.

(c) Heating

1. Thermal balance. - It is generally true that a suitable thermal balance must prevail for any given oven for economic reasons; the same reasons demand that the thermal balance of a shale retort must be equally satisfactory. This study, however, should not be based solely on averages. It should be emphasized that numerous shales present important differences in composition, in particular in oil and fixed carbon content, and these variations greatly influence the various items of the thermal balance.

The water content as well as the volume and calorific value of the evolved gases should also be taken into account. Moreover, although the exothermic heat of reaction is low, it depends, nevertheless, on the amount of oil present and cannot be neglected. The method for using the heat in the oven must also be considered.

Logically, the first step is to recover noncondensable gases and use them to heat the ovens. However, in most instances this source of heat has not been sufficient. It is natural, therefore, that the use of the fixed carbon present in the mineral residue from pyrolysis has been considered to furnish additional heat. Combustion is possible only when the fixed carbon content of the residue is not lower than 6 percent. Under these conditions, and, of course, when its carbon content is higher, the thermal balance will show an excess of usable calories. It follows, therefore, that in many cases the fixed carbon alone can furnish sufficient heat for the pyrolysis of shale, and that it is possible to obtain better utilization of the noncondensable gases. At least, this is the present tendency.

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2. Heating method. - Pyrolysis can be accomplished by applying heat either internally or externally, as in ovens for making wood charcoal.

Internal heating, in which the required heat is carried through the mass of the shale by fumes or by gases suitably preheated, is particularly convenient for treating large pieces. This procedure allows the best distribution of the heat into the product being treated. Its application a vertical oven, in which the rock travels from top to bottom by gravity, constitutes the most economical heating system. Moreover, the circulation of the gases carried out the oil as soon as it is formed, thus limiting cracking. However, dilution of the vapors of pyrolysis, rich in valuable products, into a larger volume demands the installation of large and costly condensation systems.

Internal heating is not applicable to the treatment of the fines, as the compact mass interfers with uniform circulation under moderate pressure of the combustion vapors. External heating is employed in the treatment of these fines, in which the material is moving in a retort externally heated by the combustion gases. To facilitate the transfer of heat through the poor-conducting mass of the shale it is necessary to operate in a thin layer and use a mechanical stirring device to bring the various surfaces in contact with the hot walls of the container.

(d) Yield

A good oven must yield, from shale treated therein, as much oil as possible. Yields are influenced by a number of factors, the foremost being proper temperature. It is important that secondary reactions, which may transform the initial decomposition products, be avoided. The extent to which secondary reactions take place is a function of the reaction velocity, which in turn is influenced by the temperature, the time required for the vapors to pass through the reaction zone, the amount of steam injected, the influence of the walls of the reaction chamber, and the condition of the charge. All of these factors must be controlled in order to obtain the maximum yield of crude oil. However, when conditions are such that the extent of secondary reactions is reduced to a minimum, the yield of benzine may be low. The amount of benzine is larger if the oil has been submitted to some cracking in the oven and if conditions are chosen so that secondary reactions are allowed to proceed to some extent. This increases the volume of gas formed, and the yield of crude oil is unfavorably influenced. It seem preferable to attempt first to extract from the shale the largest possible amount of oil and to crack this oil later in a separate operation, if large proportions of light carburants are desired.

These are the principal characteristics of shale ovens. Each type of oven differs by the manner in which the results are obtained. It follows that the same shale treated in different ovens will give different results. In view of the great difference in composition of shales, the choice of an oven is particularly difficult. It appears that the problem can be viewed in the light of two distinct sets of considerations: (1) Those relating to the quality of the shale to be heat-treated, and (2) those relating to the heating procedure.

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1. Shales will react under pyrolysis according to their softening tendencies. Whereas poor shales can be treated by simpler methods, such as one whereby the spent shale drops out by gravity, rich shales gnerally require apparatus designed to avoid agglomeration and caking.

Again, treatment of fines usually requires a particular technique, including arrangements for external heating, which will be described in the discussions of such ovens.

2. Although the heating procedure appears to be largely independent of the characteristics of the shale, it does depend on the quality and sales price of the combustible and the use that can be made of the residual gases. In most instances it will be more practical to burn the fixed carbon in the oven itself. But it is sometimes advantageous to carry out this combustion in a separate producer that is easier to run, the required heat being furnished, if necessary, by the combustion of cheap shale, fines, or even coal.

As these considerations are sometimes in opposition, it is desirable, before choosing an oven type, to test the shale in a unit already existing.

Classification and Description of the Principal Shale Ovens (Retorts)

Shale retorts are generally classified according to their heating procedure. We shall follow this rule and examine (1) retorts with internal heating, (2) retorts with mixed internal-external heating, and (3) retorts with external heating. In each of these classifications only the well-known and used types will be described; we shall discuss new types only if they have been submitted to industrial tests.

1. Internally heated retorts

These retorts, in which the heat necessary for pyrolysis is transported by a gaseous fluid in intimate contact with the mass under treatment, have the advantage of an excellent transfer of heat throughout the mass of shale in process. However, owing to the fact that resistance to the internal circulation of the heating fluid must remain normal, these retorts can only treat shales of such sizes that the loss of unreacted charge will be low and sufficiently uniform, that the passage of the gas be distributed uniformly. The height of the layer under treatment must also, for the same reason, be judicially limited. Finally, one must consider that the circulation of considerable volumes of gases and vapors can carry dusts even as far as the condensation system.

The main disadvantage of internally heated retorts is that they require large and costly condensation equipment, as the oil and gasoline vapors obtained by pyrolysis are diluted by a large volume of inert gases. The important disadvantage, however, is limited to a certain class of internally heated retorts. In fact, heat transfer can be carried out (1) directly in the mass to be heated, by fumes or hot gases coming from the combustion of the residual carbon or the distallation gases (retorts of this kind are of direct internally heated type), and (2) by recycling the distillation gases

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previously preheated by an exterior source of heat. These retorts are said to be of the indirect internally heated type.

In the first method there is considerable dilution of the vapors by distillation gases. In the second, however, in which the recycle gases and combustion vapors follow separate cycles, only the recycled gases are condensed. It is even possible, as in the Kivioli and Grande Pariosse retorts, to condense only the excess of the gases being recycled. The volume to be condensed is thus reduced to a minimum and allows the use of small condensation plants.

The following classification, according to increasing complexity in the gaseous cycles, has been adopted to describe these retorts.

(1) Direct internal heating

(a) LaPorta retort. - Recycled gases and carburetted air are introduced at the base of the retort.

(b) Pintsch retort. - Recycled gases are introduced alone without preheating.

(c) Fuschun retort. - Recycled gases are introduced after preheating.

(d) Roma retort.

(e) Lurgi retort. - Recycled gases, after preheating, are used partly for predrying and partly for the pyrolysis.

(2) Indirect internal heating

(f) Grande Paroisse retort. - Recycled preheated gases and stack gases flow through the shale over different circuits.

(g) Kivioli retort.

(1) Direct internally heated retorts

(a) LaPorta retort (fig. 10). - Used by Asfalti-Bitumini-Combustibili Liquidi Derivati, an Italian corporation.

This type of retort has been used in Sicily since 1918 for the treatment of poor asphaltic limestones and gives, by distillation, 6 to 12 percent oil.

As the mineral residue of Sicilian asphaltic limestone contains very little fixed carbon after distillation of the oil, the LaPorta retort, the elevation of which is similar to that of a lime kiln, has been designed so that combustion of a part of the bituminous substances of the rock will furnish the heat necessary for pyrolysis of the remainder. This process, which resembles the Meiler wood-carbonization process, in which some of the wood is burned in order to carbonize the rest, is justified in Sicily, where rock

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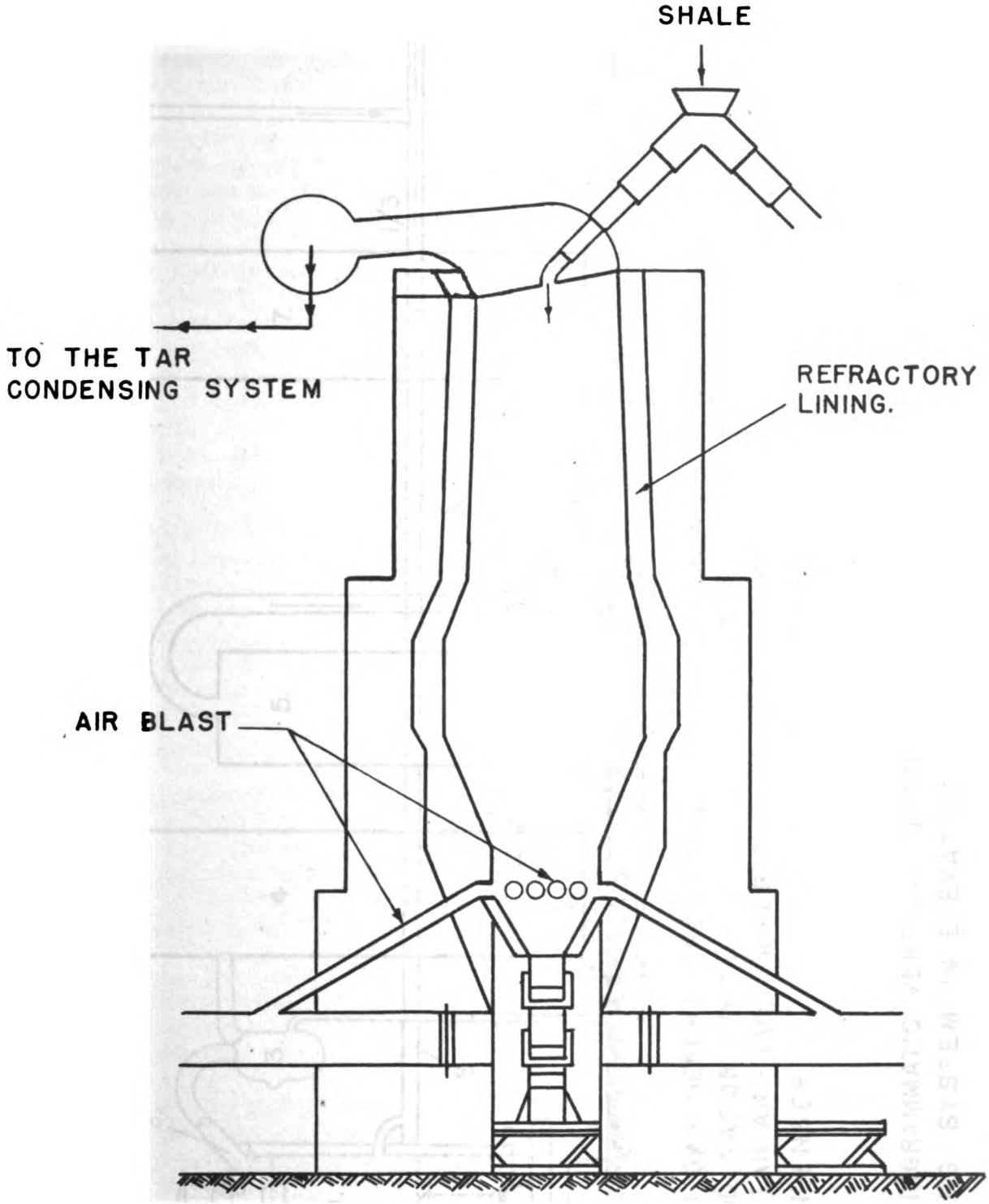

FIG. 10. LA PORTA RETORT, DIAGRAMMATIC VERTICAL SECTION.

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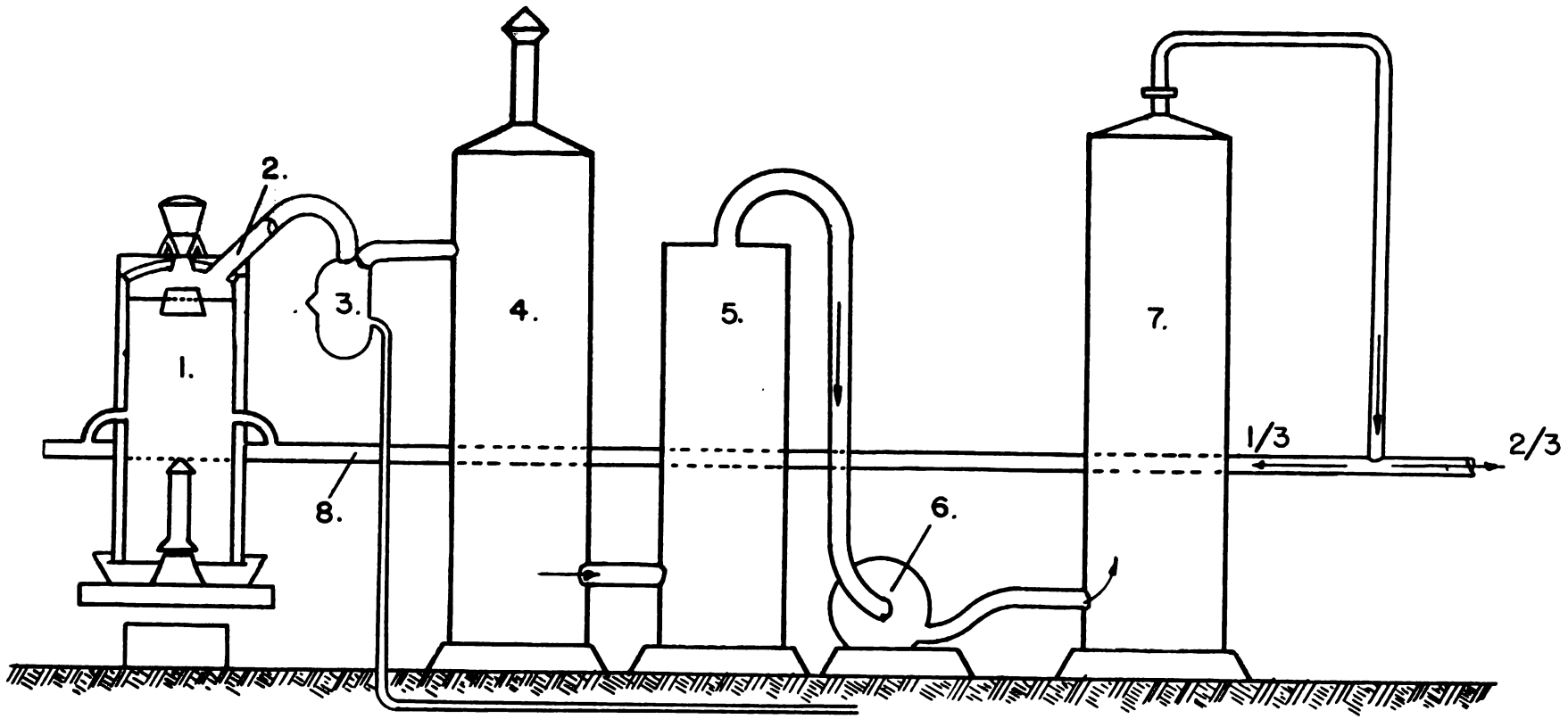

1. PINTSCH GAS GENERATOR (RETORT)
2. GAS AND VAPOR OFF TAKE
3. HEAVY TAR AND DUST SEPERATOR
4. AIR CONDENSER
5. SCRUBBER CONDENSER
6. GAS EXHAUSTER
7. SCRUBBER FOR LIGHT HYDROCARBONS
8. RECYCLE GAS

FIG. 11. DIAGRAMMATIC VERTICAL SECTIONAL VIEW OF THE PINTSCH RETORT WITH CONDENSING SYSTEM IN ELEVATION.

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extraction is cheap and no other combustible is available. Oils costing 4,000 francs a ton could not be used as combustible in France.

In the LaPorta retort the rock drops by gravity from the top to the bottom, and the mixture of air and recycled gas circulates countercurrently. This mixture, injected at the base of the retort at a temperature of 120° C., will be heated by the spent shale, which is thus cooled before being removed.

The gaseous mixture then passes through a layer still containing some organic matter, which burns in contact with the air present and the heat generated, which may raise the temperature of the shale to 750° C., promotes distillation of the cool shale in the layer situated immediately above. Carrying the distillation vapors, the gases then give up a part of their heat to the fresh shale and leave the oven at a temperature of 80° C. enroute to the condensation plant. After removal of condensable vapors, some of the gas is recycled to the oven, the remainder being discharged to the stack. Four zones thus are formed:

	°C.
1. Preheating and drying.....	70-200
2. Distillation.....	200-450
3. Combustion.....	450-750
4. Cooling of the residue and recovery of its sensible heat.	

Owing to the low temperature of the gases coming out of the retort, some entrainment of the oil takes place as well as some retrogradation of the heavy fractions in the hot zone, where cracking harmful to oil yield takes place.

The thermal balance assumes that about one-third of the oil contained in the mineral is burned to furnish the heat necessary for distillation and that two-thirds only are recovered in the form of salable products. In Sicily, the mineral composition of the rock permits utilization of the residues in the manufacture of cement. The temperature must not be raised above 750° C. to avoid decomposition of the limestone, which is endothermic.

To summarize, the LaPorta retort permits treatment, without consumption of fuel from other sources, of poor asphaltic limestone found locally, but the low oil yield limits its use to very special conditions, such as the Sicilian exploitation.

(b) The Pintsch retort, which is used in Estonia for the pyrolysis of kukersites rich in oil, has the general appearance of a gas producer. It employs direct internal heating. Figure 11 is a diagrammatic vertical section of a Pintsch retort.

Gasification of residual carbon in the lower interior zone furnishes to the upper layers the heat necessary for pyrolysis of crude shale.

The Pintsch retort is a vertical cylinder of 2.25 m. (7.4 feet) interior diameter and 6.15 m. (20.2 feet) height made of sheet iron lined with

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refractories. The shale broken to 40 to 175 mm. (1.6 to 7.0 inches) flows by gravity. The ease with which the kukersite softens and agglomerates, forming clinkers that block passage to gases and heat transfer, constitutes the principal problem. It has been solved partly by allowing the rock to travel downward at a very rapid rate so as to reduce the time over the hot region; also, by following a more careful classification of the shale sizes. This has been done by putting a cone below the charging hopper. The pieces will either slide or bounce onto the cone, according to their dimensions, and fall into the oven, the large ones going to the middle and the smaller ones to the edge. This disposition, by assuring more even passage of the gas, avoids local overheating. The shale remains in the oven 12 hours. The residues are removed dry by means of a revolving bottom, an arrangement similar to those used in gas producers. Combustion of the residual carbon is effected by injecting air at the base of the oven. However, to avoid rising temperature in the pyrolysis zone, which might cause softening, there is also injected, somewhat above the air ports, about one-third of the mixture of distillation gas and vapors, which arrive, cooled, from the condensers.

In this oven (of simple construction and low cost) the yield of oil is about 80 to 90 percent of that obtained with the Fischer retort.

(c) The Fuschun retort (figure 12) is used in Manchuria for the pyrolysis of poor shale containing 5 to 6 percent oil. It is based upon the same principle as gas producers for the recovery of tar and consists of two cylindrical sheet-iron receptacles lined with refractories, which are superimposed and connected by a narrow section in the form of a truncated cone. The fixed carbon is burned in the lower receptacle by injection of steam and air, and the resulting gases pass through the upper section, which functions as a distillation retort. Thus the shale mass is heated internally.

Owing to the low fixed-carbon content (about 4 percent), the gas furnished by the lower section is insufficient to effect complete pyrolysis of the shale. Consequently, some of the distillation gases are recycled at the base of this retort after being freed from condensable vapors and reheated. This reheating, which is accomplished by the combustion of another fraction of the distillation gases in a superheater, is consequently carried out externally.

The distillation retort has an inside diameter of 2.6 m. (8.5 feet). Its volume of 20 cubic meters (706 cubic feet) corresponds to 20 metric tons (22 short tons) of shale broken to 10 to 75 mm. (0.4 to 3 inches). For a production of 50 metric tons (55 short tons) per day, the shale remains 3.2 hours in the distillation zone. The producer gas and recycled gas reach the distillation retort at a temperature of 550° to 650° C., drop to 450° to 500° C. in the distillation zone, and emerge from the oven at 150° C. For the pyrolysis of 1 kg. (2.2 pounds) of Fuschun shale, 200,000 calories, of which 50 percent are furnished by the gas producer, are necessary. This is equivalent to approximately 720,000 B.t.u. per short ton. The yield in oil is about 95 percent of the Fischer assay.

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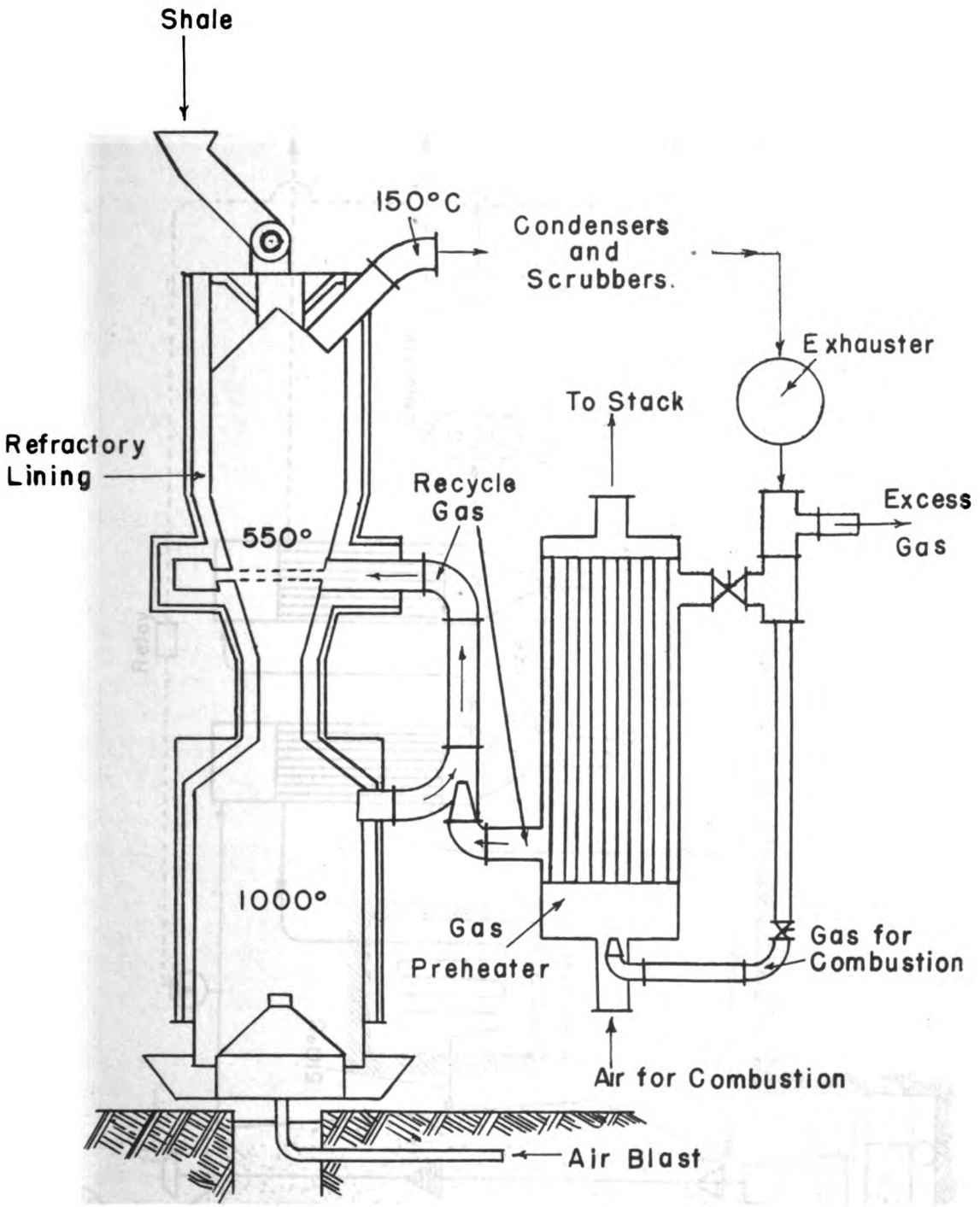

FIG. 12. DIAGRAMMATIC VERTICAL SECTION OF THE FUSCHUN RETORT.

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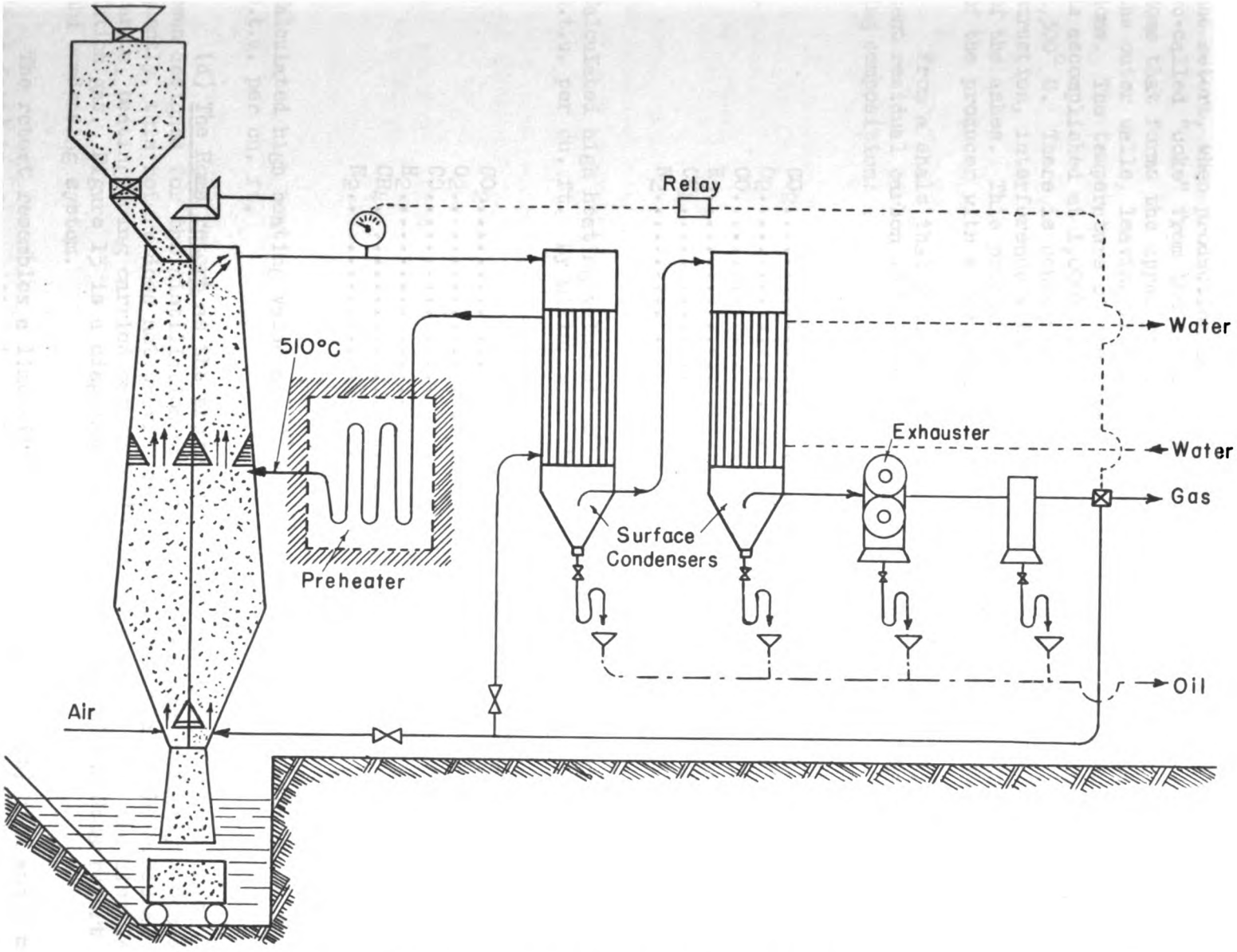

FIG. 13. DIAGRAMMATIC SECTIONAL VIEW OF THE ROMA RETORT AND CONDENSING SYSTEM.

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The producer section has an inside diameter of 3 m. (9.85 feet); its volume is 27 cubic meters (953 cubic feet). The shale remains 15 hours in the retort, when production is 50 metric tons (55 short tons) per day. The so-called "coke" from the distillation section drops into a perforated brick dome that forms the upper portion of the gas producer. It is piled against the outer walls, leaving free passage for the gases under the top of the dome. The temperature of the "coke" is 500° C. The gasification reaction is accomplished at 1,000° C. The Fuschun-shale mineral residue melts at 1,300° C. There is consequently a possibility, by fusion of the ash, of obstruction, interference with the gasification, and difficulty of extraction of the ashes. This problem has been solved by providing the lower portion of the producer with a revolving bottom similar to that of the Mond producer.

From a shale that yields 6 percent oil, a "coke" containing about 6 percent residual carbon is obtained, giving, in a producer, a gas of the following composition:

	Percent by volume
CO_2	17.5
O_2	0.2
CO	6.0
H_2	15.5
CH_4	2.5
N_2	58.3
	100.0

Calculated high heating value at 60° F., 30 inches Hg., saturated - 93.3 B.t.u. per cu. ft. By mixing with the recycled gas, these values become:

	Percent by volume
CO_2	20.0
O_2	0.2
CO	5.5
H_2	18.0
CH_4	6.0
N_2	50.3
	100.0

Calculated high heating value at 60° F., 30 inches Hg., saturated - 134.5 B.t.u. per cu. ft.

(d) The Roma retort as the previously described LaPorta retort, has been designed for the distillation of asphaltic limestone of Sicily. Consequently, this retort does not provide for the gasification of the residual carbon, heating being carried out entirely by the combustion of the distillation gas. Figure 13 is a diagrammatic sectional view of the Roma retort and condensing system.

The retort resembles a lime kiln, being 12 m. (39.4 feet) high and 2 m. (6.56 feet) in average diameter. The gaseous distillation products leave the top of the retort and, after condensation, part of them are sent to the

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base of the retort, where they are burned, and part, after reheating to 510° C., to the central zone. Throughput is 210 metric tons (231 short tons) per day, and the yield equals 85 percent of the Fischer-assay yield.

The Roma retort has been used with success in carbonizing the cakes left after extraction of olive oil.

(e) Lurgi retort. - Figure 14 is a diagrammatic sectional view of a Lurgi retort showing the gas-circulating system. This retort, which is internally directly heated, is composed of two rectangular, superimposed, and distinct sections, each 5.6 m. by 3 m. (18.4 by 9.85 feet) in horizontal sectional dimensions. One of the sections constitutes the drying chamber, A, and the other the pyrolysis chamber, B, to which is attached chamber C for combustion of the residual carbon and cooling of spent shale. The distillation gases mixed with gaseous products of combustion are withdrawn at about the middle of the retort, above the pyrolysis chamber, and led to the condensation units. The cold noncondensable gases are recycled as follows:

A fraction is sent to a burner placed beside the drying chamber, to which a fan sends the combustion gases and circulates them in a closed circuit. The excess of the recycling is rejected to the atmosphere with a mixture of water vapor and hydrogen sulfide evolved from the crude shale. The average temperature attained by the shale in the drying chamber is 150° C.

Another portion of the noncondensable gases is sent to a burner placed beside the pyrolysis chamber. The gases thus produced are directed into the middle of the mass under treatment, thus providing the necessary heat. A third fraction of the noncondensable gases is conducted to the base of the retort as a coolant, where it recovers the heat of the spent shale; it is then conducted to the pyrolysis zone, where it regulates (moderates), more or less according to the amount furnished, the temperature of the gases coming from other parts in the zone.

The Lurgi retort is of simple construction and operation. It has a high throughput - about 300 metric tons (330 short tons) per day. Its yield of oil is about 94 percent of that obtained by the Fischer test.

(2) Indirect internally heated retorts

(f) Grande Paroisse retort. - Figure 7 is a diagrammatic sectional view of the Lantz retort of the Grande Paroisse with gas-circulating systems. In this retort pyrolysis of the shale is accomplished by its own distillation gas taken as it leaves the retort and recycled after reheating without having been submitted to intermediate cooling. The necessary heat for reheating the gas is obtained from a heat exchanger, which obtains heat energy through combustion of the excess noncondensable gases plus producer gas. The products from this combustion and the distillation gases follow two separate circuits as shown in figure 7.

The apparatus consists of a vertical tower, A, made of special sheet iron, of rectangular section, divided into two compartments by a suitable

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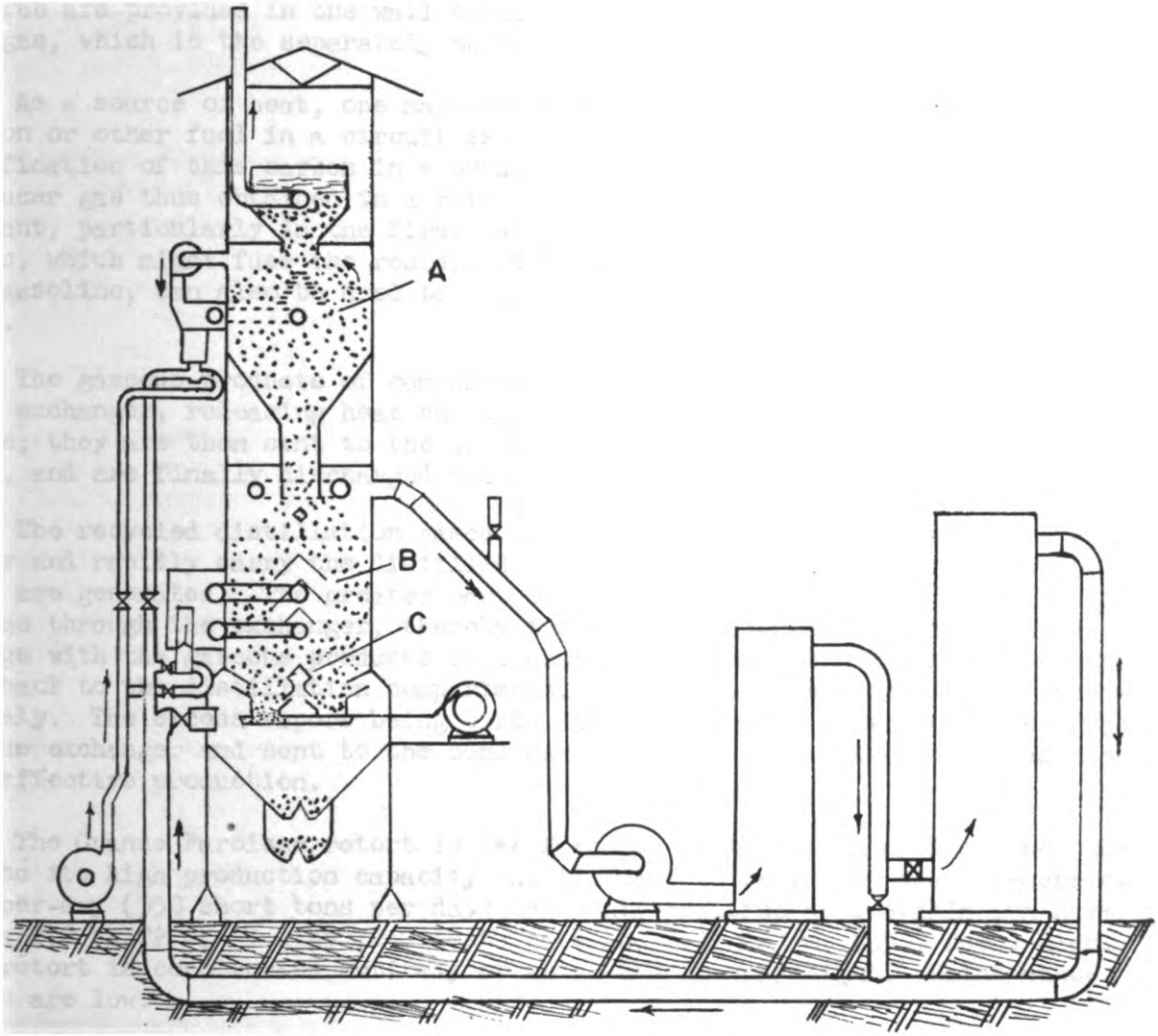

FIG. 14. DIAGRAMMATIC SECTIONAL VIEW OF A LURGI RETORT; CIRCULATING SYSTEM SHOWN IN ELEVATION.

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narrow section, B, which allows the shale to go through, but the resistance of which will prevent passage of the gas from one compartment to the other. In operation, shale broken to 4 to 60 mm. (0.16 to 2.4 inches) flows downward by gravity successively through the drying and preheating compartment, C, wherein the shale attains a temperature of 180° to 200° C., and a pyrolysis compartment, D, in which the shale is heated to 430° to 460° C. Special louvres are provided in the wall to allow horizontal circulation of the heating gas, which is the separately heated shale gas liberated in the process.

As a source of heat, one may use either the heat of combustion of residual carbon or other fuel in a circuit especially provided, or the gas from the gasification of this carbon in a producer, followed by the combustion of the producer gas thus obtained in a refractory brick-lined chamber. It is important, particularly in the first case, to avoid unnecessarily high temperatures, which might fuse the residue. The distillation gas, after removal of the gasoline, can also be used to furnish an important part of the necessary heat.

The gaseous products of combustion, at a temperature of 750° C., enter a heat exchanger, releasing heat energy to the separate circuit of distillation gases; they are then sent to the drying-preheating compartment, yielding more heat, and are finally discharged into the atmosphere.

The recycled distillation gases cross the pyrolysis compartment horizontally and rapidly carry the distilled products away from the hot zone where they are generated. The greater part of these gases, without being cooled, passes through the exchanger, thereby increasing in temperature by heat exchange with the gaseous products of combustion, and go through this apparatus and back to the distillation compartment, and follow this closed cycle indefinitely. The excess vapors being circulated are removed from the cycle ahead of the exchanger and sent to the condensation plant. This excess represents the effective production.

The Grande Paroisse retort is the foremost installation of its type, owing to its high production capacity and its ease of operation - a 500-metric-ton-per-day (550 short tons per day) oven only requires an installation having a 2.2 by 22 m. (7.2 by 72.2 feet) base and being 17 m. (55.7 feet) high. The retort is constructed entirely of metal and is very tight. Maintenance costs are low.

Distillation gases are not diluted, and the portion recycled is not cooled; condensation apparatus and water are used to a minimum, as they need only treat the 25 to 30 cubic meters of gas that is the average yield per metric ton of shale (900 cubic feet at 60° F., 30 inches Hg., saturated, per short ton).

Owing to the low volume of gas to be treated, removal of benzine is much easier and the yield is improved.

The consumption of heat energy (calories) per metric ton of shale is lower than 250,000 kg.-calories (902,000 B.t.u. per short ton), consequently,

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the thermal yield is 55 to 60 percent. Regarding the total yield, as soon as formed the distillation products are swept out of the 430° C. to 460° C. zone, where they originate by means of the horizontal gaseous current. Thus, there is very little chance of immediate degradation. The question has been raised, however, whether or not the recycling of gases, whereby unstable products are brought back into the reheater where the temperature is high, favors cracking. Analytical results seem to indicate that it does not.

Finally, the yield in oil amounts to at least 95 percent of the Fischer assay retort test.

(g) Kivioli tunnel oven. - Figures 15, 16, and 17 are different views of the Kivioli tunnel oven. In common with the Grande Paroisse retort, the Kivioli oven utilizes the gas from distillation as the heat vehicle between the source of heat and the shale to be heated. It was designed to overcome difficulties resulting from the caking tendencies of the Estonian kukersites. The shale circulates through the interior of a horizontal retort in small cars without collision, hence the name "tunnel" oven given to this installation.

To treat 400 metric tons (440 short tons) per day, the cylindrical retort forming the tunnel has to be 53 m. (174 feet) long and 2 m. (6.56 feet) in diameter. It is divided into three successive zones - drying, distillation, and quenching - separated into sections by double sliding doors, which prevent passage of the gas from one zone to another. These sections are ventilated to prevent formation of explosive mixtures resulting from accidental ingress of air. The danger is small, however, as the retort operates under a pressure of 150 mm. water, equivalent to 5.9 inches. Each car carries 2.2 metric tons (2.42 short tons) of shale in walnut-size pieces, the thickness of the layer thus being about 900 mm. (35.4 inches). The oven contains 17 such cars - 3 in the drying zone, 12 in the distillation zone, and 2 in the cooling and quenching zone. The cars are moved every 8 minutes; consequently, the shale will remain 96 minutes in the distillation zone of the oven.

Each displacement places one car above the heating-gas opening. This heating gas travels perpendicularly through the shale and escapes immediately through an orifice diametrically opposite, sweeping with it either the drying vapors or the products of distillation.

Drying is carried out by recycling after reheating the steam obtained from the 6 to 9 percent moisture present in the crude shale. Vapors are circulated by a fan. The vapors first pass through an externally heated tubular superheater, then through the drying section, which the gases enter from the top and from which they are removed, rich in vapors, at the bottom. The vapor excess is evacuated into the atmosphere, which thus cuts down the load on the oil-condensation installation. There are three parallel circuits, each corresponding to a car.

In the distillation zone, by a similar process, the gases heated in an externally heated superheater-oven, circulated by a fan, passed through the retort from bottom to top and promoted pyrolysis of the shale, immediately

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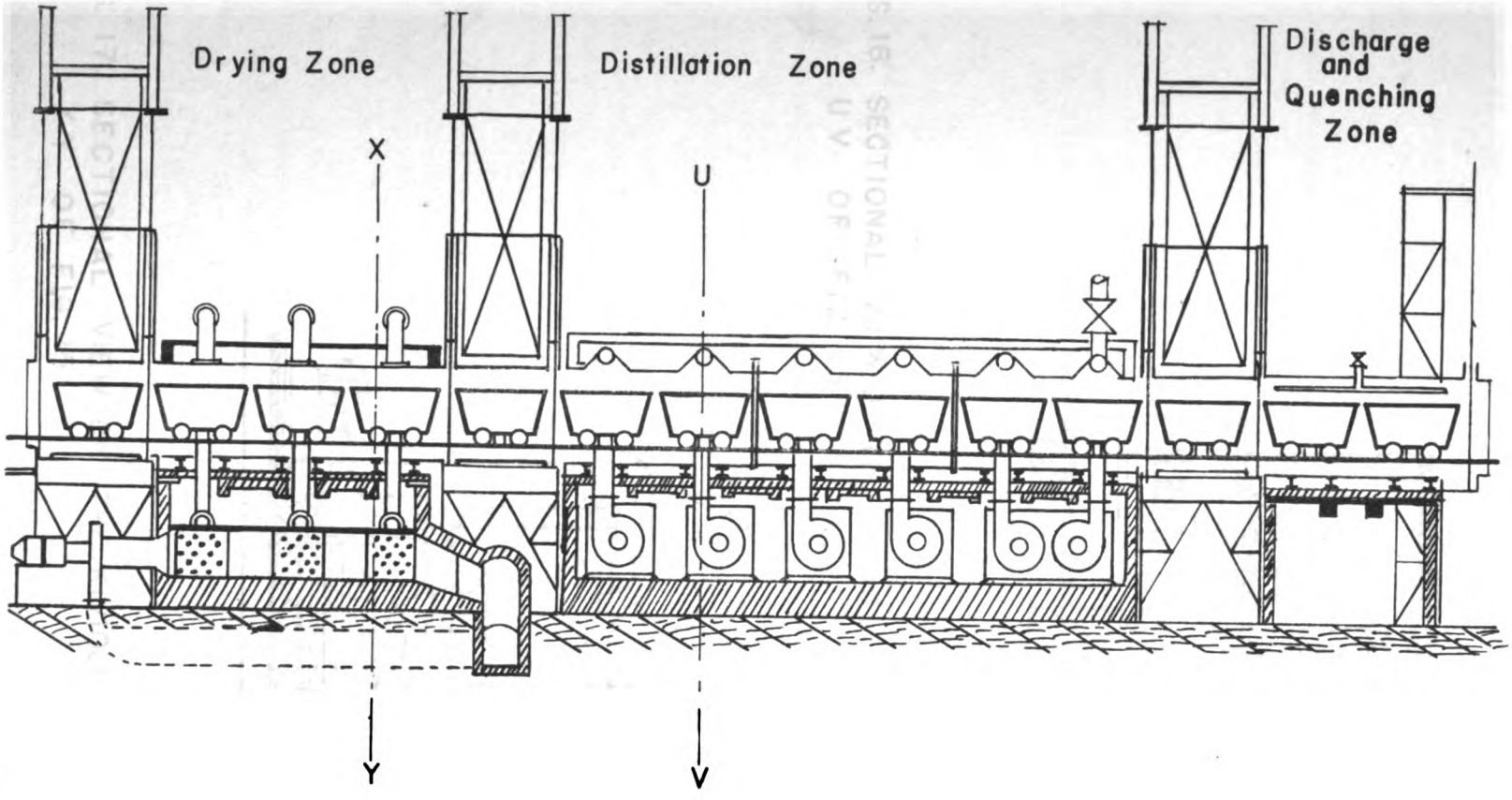

FIG. 15. LONGITUDINAL VIEW OF THE TUNNEL (KIVIOLI) OVEN.

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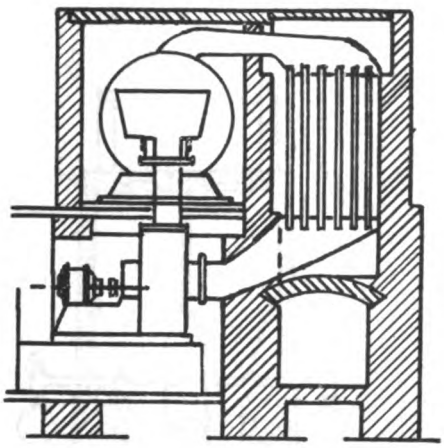

FIG. 16. SECTIONAL VIEW OF THE KIVIOLI OVEN, THROUGH U V OF FIG. 15.

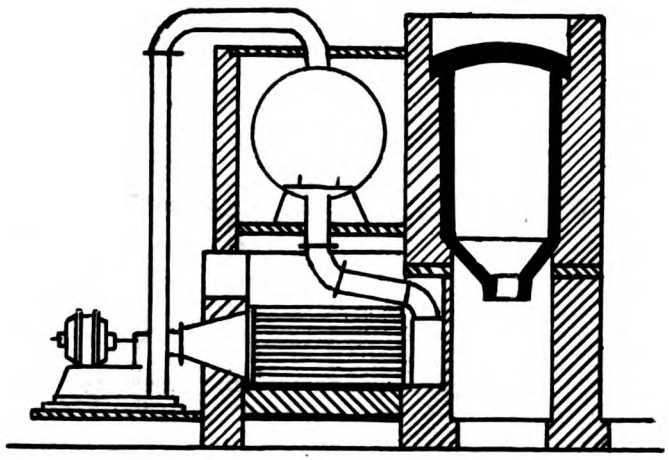

FIG. 17. SECTIONAL VIEW OF THE KIVIOLI OVEN, THROUGH X Y OF FIG. 15.

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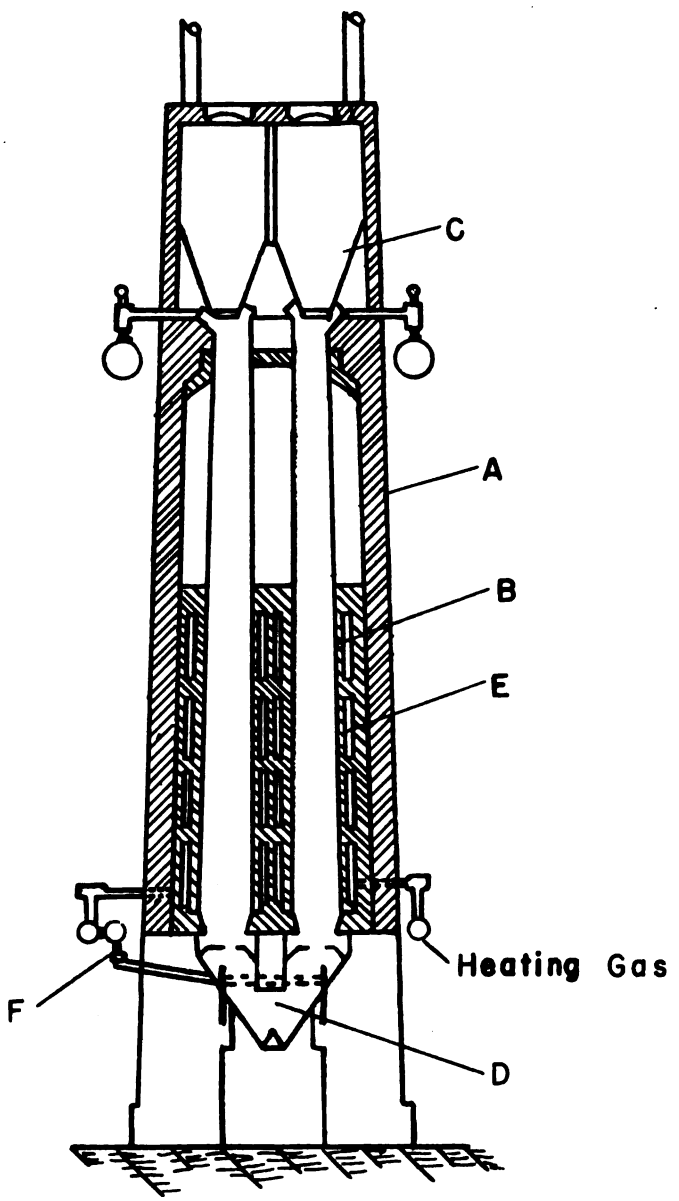

FIG. 18. DIAGRAMMATIC SECTIONAL VIEW OF A PUMPHERSTON RETORT.

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carrying away the distillation products. Before closing the cycle by sending the vapors back to the superheater, the excess gas is removed and sent to the condensation plant for recovery of valuable products. Many parallel circuits of cars may be under treatment.

The gas-inlet temperature in the retort is distributed from 350° to 475° C., according to the circuit under consideration. The outlet temperatures are 175° to 450° C. In the third zone the shale is cooled by sprinkling with water before removal. Heat is produced in the central furnace, where shale pieces less than 10 mm. (0.4 inch) in size are being burned. A combustion chamber placed beside this furnace is used to burn noncondensable gases. The gaseous products of combustion, which have a temperature of 1,600° C., are partly diluted by those used for heating the oven so as to lower their temperature to 950° C. The mixture furnished the necessary heat first to the distillation chamber and then to the drying-section superheaters. At the end of the circuit, the gas temperatures are reduced to 250° C. but can still be used for an exterior predrying of the shale, which lowers their temperature to 75° to 100° C.

The yield of the Kivioli oven is 94 to 99 percent of the Fischer assay yield. However, its upkeep is costly owing to its complex mechanical construction. In practice it operates only 20 days per month, the other 10 days being used for repairs. It is well designed for the treatment of the kukersites, however, which are difficult to handle.

2. Mixed internal and external heating ovens or retorts

This type of oven is represented by the various Scotch retorts, which have been favored for a long time by industry before the competition by the new internal heating ovens.

Pumpherston retort. - This retort, which is the classical Scottish type, is the oldest retort used in the shale industry, not only in Scotland, where it originated, but also in France, where this type, continuously improved, has been used for a long time in the Autun plant of the Ste. Miniere des Schistes Bitumineux. Figure 18 is a diagrammatic sectional view of a Pumherston retort.

The Pumpherston retort consists essentially of two distinct and superimposed sections: (1) A low-temperature distillation section consisting of a vertical cast-iron retort A, in which the shale temperature is raised to 450° to 550° C. and where the actual distillation is carried out, and (2) a gas-producer section consisting of a refractory-brick vertical retort, B, in which the fixed carbon is gasified at a temperature that may reach 1,000° C. by means of steam and air, with the production of ammonia.

Both sections form a vertical oven 18 m. (59 feet) high, including the cast-iron retort A, which is slightly conical, 4.5 m. (14.7 feet) high, and 0.7 m. (2.3 feet) average diameter; the refractory brick retort B, which is also slightly conical, 5.5 m. (18 feet) high, and 0.5 m. (1.6 feet) average diameter; a loading screen, C; and an unloading screen, D.

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Heating is partly external. Gases produced in the retort burn in openings E, surrounding the oven; the vapors are evacuated on the outside.

For the extra heat, limited internal combustion is carried out by injecting a certain quantity of steam and air at the base of the refractory retort, F. The mixture of steam and air passing through the oven zone, which functions as a producer, reacts with the fixed carbon of the residue and produces water gas. The gas stream continues its upward path in the cast-iron retort through the mass of the shale being distilled, supplying additional heat, and, through its hydrogen content, contributes to the transformation of the greater part of the nitrogen into ammonia.

The retorts are set in groups of four, and a battery includes 40 retorts. The length of passage of a charge is 36 hours. Throughput of each retort is thus 3.5 to 4 metric tons (3.8 to 4.4 short tons) per 24 hours; it can be increased to 6 and even 10 metric tons (6.6 to 11 short tons) per 24 hours by careful injection of steam and air. However, the Pumpherston oven throughput is low compared to its size. It is cumbersome and requires a large initial investment. It is only suitable for the treatment of fairly large pieces. Fines distill poorly, lower the yield, and facilitate cracking. However, its construction is simple and sturdy and its operation is easy. The yield is 85 to 90 percent of the Fischer assay yield, and the thermal balance recently has been improved by the use of stack gases for the production of steam. Finally, it allows the recovery, as ammonium sulfate, of 80 percent of the nitrogen present in the shale, which amounts to about 12 to 15 kg. of ammonium sulfate per metric ton (27 pounds per short ton) of shale. It is not suitable for treating either very poor or very rich shales, but it is best adapted to the pyrolysis of shales of average oil content.

This concludes the translated French report.

The Pumpherston retort, which was used for years without internal heating through the introduction of air into the shale being processed, is typical of externally heated retorts; this class of retort has not been separately considered in the foregoing.

SHALE DEVELOPMENTS IN ESTONIA

GERMAN-ESTONIAN SHALE-OIL PRODUCTION

According to captured documents, the Germans became seriously interested in Estonian shale-oil recovery early in 1942. It appears that their inability to capture the Russian oil fields was already apparent to them, and that development in Estonia, where by heat treatment the oil shale yields as much as 20 percent of oil, might be of great importance to them. It soon became imperative that the Estonian deposits be exploited to supply the German military requirements. For this purpose, German technologists were called on to plan a course of action. They recognized that difficulties had to be overcome, but in view of the high oil yield (20 percent) that could be obtained from Estonian shale, it was considered that the annual production of oil from that source should be at the rate of 200,000 metric tons (220,400 short

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tons) by the end of 1942, 370,000 metric tons (407,700 short tons) by the end of 1943, and 560,000 to 600,000 metric tons (635,000 short tons) by the end of 1944. It was considered that the works at Jarve should contribute about 210,000 metric tons. A metric ton (2,200 pounds) of free shale was said to cost 3 to 4 Reichsmarks, and the fuel oil could be sold for 51 Reichsmarks per metric ton ($20.40, based on a 40-cent mark).

Data available at that time were not reliable as to gas composition but seemed to be more dependable in respect to product distribution. The following products were considered to be obtainable from shale oil:

	Percent by volume
Benzine	12.0
Tractor fuel	4.0
Diesel fuel (middle oil)	27.0
Heating oil (fuel oil)	37.0
Bitumen	17.5
Loss	2.5
	100.0

Until that time, only about 10 percent benzine had been separated, as well as small amounts of bitumen, so that almost the entire bulk had been recovered as fuel oil. The latter, of course, contained a large amount of asphalt.

The recovered benzine (boiling range not well established at that time) contained 62 percent of unsaturates and had a very good knock rating. The Diesel-oil fraction contained about 50 percent of unsaturates and was used as power fuel in Estonia. The German Navy apparently had contracted to purchase about 200,000 to 250,000 metric tons (220,000 to 275,000 short tons) per year of fuel oil and would take additional amounts when available. The asphalt, it was believed, could be used for roads in the Baltic States as well as for the manufacture of electrode carbons.

At a subsequent meeting of the German technologists, plans for future development of the Estonian shale by the Germans were outlined in much greater detail; they included the following:

Plant Capacity

When the plant-expansion program was completed, the annual capacity for producing shale oil was to be 590,000 metric tons (649,000 short tons) per year. In the final plan, this single plant group (six plants) was referred to as Plant No. 1. Details are given later on in this paper. According to information otherwise obtained, the final and complete plans were much more extensive and included provisions for future annual production of an additional million metric tons, or a total of about 1.5 million metric tons (1.65 million short tons).

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Oven Systems

Until that time, the Pintsch generator (retort) had a capacity of 35 to 40 metric tons (38.5 to 44 short tons) of shale per day. A 100-metric ton (110-short ton) unit was to be tested in Works 3 (Kochtla) in the spring of 1943. It was planned to use the larger units in Works 6. Such a unit generates 650 cubic meters of gas per metric ton (22,340 cubic feet per short ton, at 60° F., 30 inches Hg., saturated) of shale. The principal disadvantages of the Pintsch retort are the destruction of valuable byproducts such as benzine, gas oil, H_2S, acetone, etc., and the large volumes of gas to be handled.

The tunnel ovens were first built in units of 200 to 250 metric tons (220 to 275 short tons) capacity per day and later in units of 400 metric tons (440 short tons) per day capacity. Gas production is only 25 cubic meters per metric ton (857 cubic feet at 60° F., 30 inches Hg., saturated, per short ton) of shale. The recovery of valuable byproducts from such small volumes of gas is quite easy. It was planned to use both types of ovens (three Pintsch retorts for each of the tunnel ovens installed, so that half of the production would be from each type) whereby the tunnel ovens would be heated by gas from the Pintsch retorts. This would save the heating oil previously used in heating the tunnel ovens.

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Shale-treating works of plant 1/

Location	Oven systems	Number at end	Short tons crude oil produced: 1940, before destruction	Short tons crude oil produced: May 1942	Short tons crude oil produced: End 1943, end of building program	Power supply
1. Kivioli (German)	Tunnel.....	6	77,000	Began in middle 1942	134,000	From Narva.
	Pintsch.....	6 + 2	-		47,000	
					181,000	
2. Kütte Joud 2/	-	-	-	-	-	-
3. Kochtla Jarve (State)	Tunnel.....	2	66,000	44,000	57,000	Own plant rebuilt.
	Pintsch.....	50	-	-	3/ 124,000	
					181,000	
4. Sillama 4/ (Sillamagi) (Swedish)	Tunnel.....	2	44,000	-	44,000 (Fall 1942)	Outside source.
	Pintsch.....	-	-	-		
5. Kochtla (English)	Davidson rotating oven	8	12,000	5,500	12,100 (Fall 1942)	Outside source.
6. Jave 5/ (newly built)	Tunnel.....	4	-	-	114,000	Own plant.
	Pintsch.....	15 + 3	-	-	115,000	
					229,000	
Total.....			199,000	49,500	647,100	

1/ All works lack cooling soft water.
2/ Shale for sale to other industries only.
3/ Includes 7,700 short tons per year of benzine from gas oil washing (fall 1943).
4/ Works 4 had port facilities for 2,000-ton vessels.
5/ Works 6 was built on a lake.

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Some of the technologists favored building only tunnel ovens for reasons based upon the above objections to the Pintsch retort, as well as (after surmounting the various technical difficulties) because of the possibility of replacing the heavy oil by heating the ovens with shale or shale generator gas. No agreement was reached at that time among the technologists concerned, owing to lack of technical data. Both oven systems were to be installed in Plant 2.

Following is a comparison of the oven systems.

Comparison of oven systems, Pintsch retorts

		Tunnel ovens	
		With fuel-oil heating	With Pintsch retort gas heating
Throughput, short tons shale per day	Present, 38-44; planned, 110	440	440
Heating fuel	Own gas(excess)	Heavy oil 17 to 20 percent of the crude oil	Own gas plus excess Pintsch gas
Products:			
Benzine[a]	15	29	29
Middle oil[a]	41	46	46
Heavy oil[a]	64	)fuel	61
Asphalt and pitch[a]	64	85)oil	59
	184	160	195
Gas oil[b] from stabilization	0.5	1.5	1.5
Gas oil from pyrolysis gas	-	2.0	-
Pyrolysis gas, cubic meters per metric ton of shale (cubic feet per short ton of shale, 60° F., 30 inches Hg., saturated)	650 (22,300)	22-25 (755-860)	22-25 (755-860)
Benzine hydrocarbons in heating gas, grams per cubic meter	20	10	10
(pounds per 1,000 cubic feet)	(1.16)	(.58)	(.58)
Moisture content of original material, percent	At the mine: 10-12	As used, 6	
Carbonization water:			
Ratio of crude oil to water	1 to 0.63	1 to 0.30	
Water[a]	120	50	
Reaction of the water	Strongly acid with HCl, H_2SO_4	Weakly acid	
Phenol content of the water	Unknown	Unknown	

a/ Kilograms per metric ton of shale or pounds per 1,000 pounds.
b/ Can be recovered; not done at that time.

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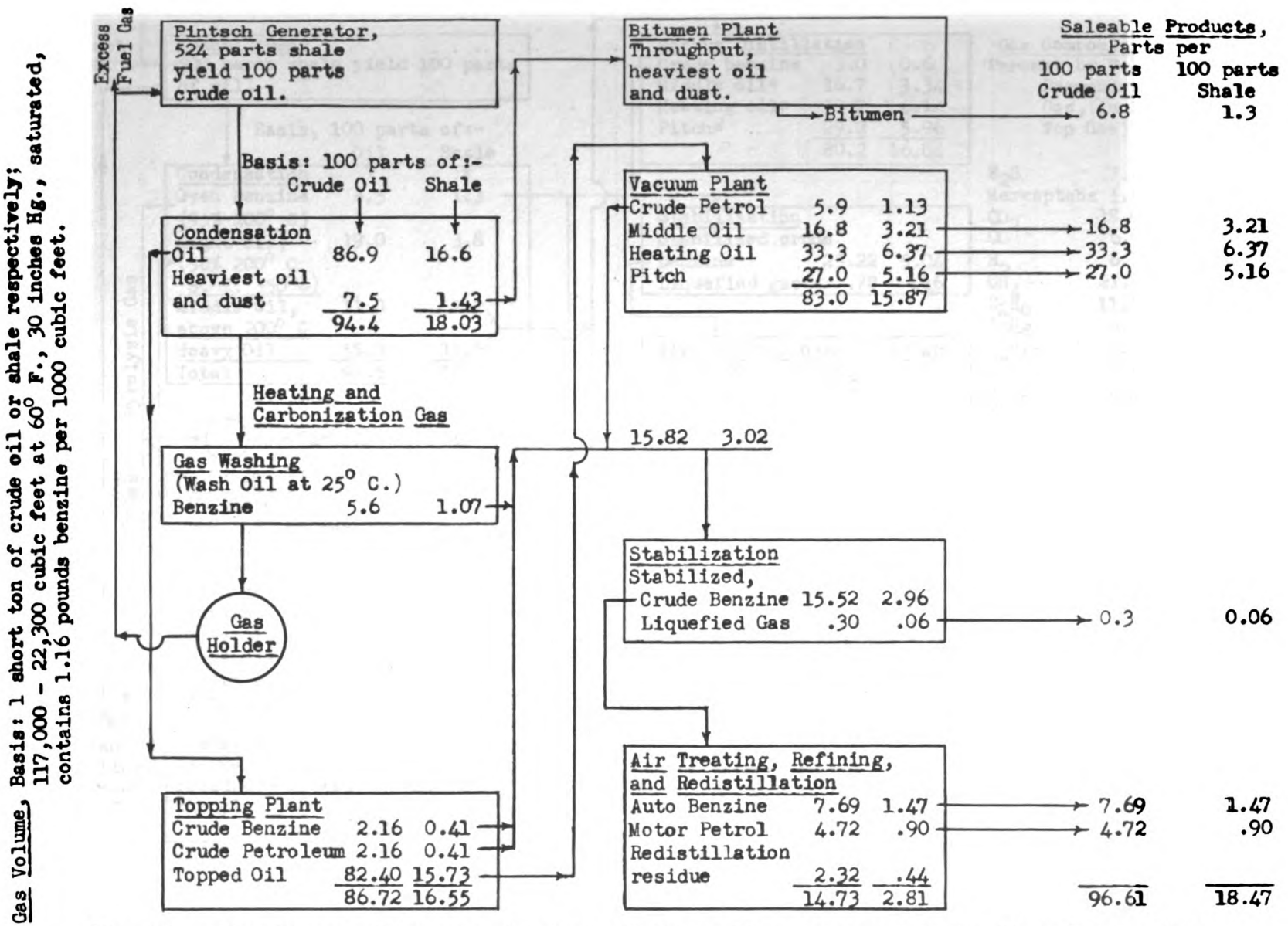
Gas Volume, Basis: 1 short ton of crude oil or shale respectively; 117,000 - 22,300 cubic feet at 60° F., 30 inches Hg., saturated, contains 1.16 pounds benzine per 1000 cubic feet.
Excess Fuel Gas
Pintsch Generator, 524 parts shale yield 100 parts crude oil.
Basis: 100 parts of:- Crude Oil Shale
Condensation
Oil 86.9 16.6
Heaviest oil and dust 7.5 1.43
94.4 18.03
Heating and Carbonization Gas
Gas Washing
(Wash Oil at 25° C.)
Benzine 5.6 1.07
Gas Holder
Topping Plant
Crude Benzine 2.16 0.41
Crude Petroleum 2.16 0.41
Topped Oil 82.40 15.73
86.72 16.55
Bitumen Plant Throughput, heaviest oil and dust.
Bitumen
Vacuum Plant
Crude Petrol 5.9 1.13
Middle Oil 16.8 3.21
Heating Oil 33.3 6.37
Pitch 27.0 5.16
83.0 15.87
15.82 3.02
Stabilization
Stabilized,
Crude Benzine 15.52 2.96
Liquefied Gas .30 .06
Air Treating, Refining, and Redistillation
Auto Benzine 7.69 1.47
Motor Petrol 4.72 .90
Redistillation residue 2.32 .44
14.73 2.81
Saleable Products, Parts per
100 parts Crude Oil 100 parts Shale
Bitumen 6.8 1.3
16.8 3.21
33.3 6.37
27.0 5.16
0.3 0.06
7.69 1.47
4.72 .90
96.61 18.47

Fig. 19. - Flow diagram showing treatment of oil from a Pintsch retort plant. Pintsch generator with (planned) vacuum distillation (Kivioli).

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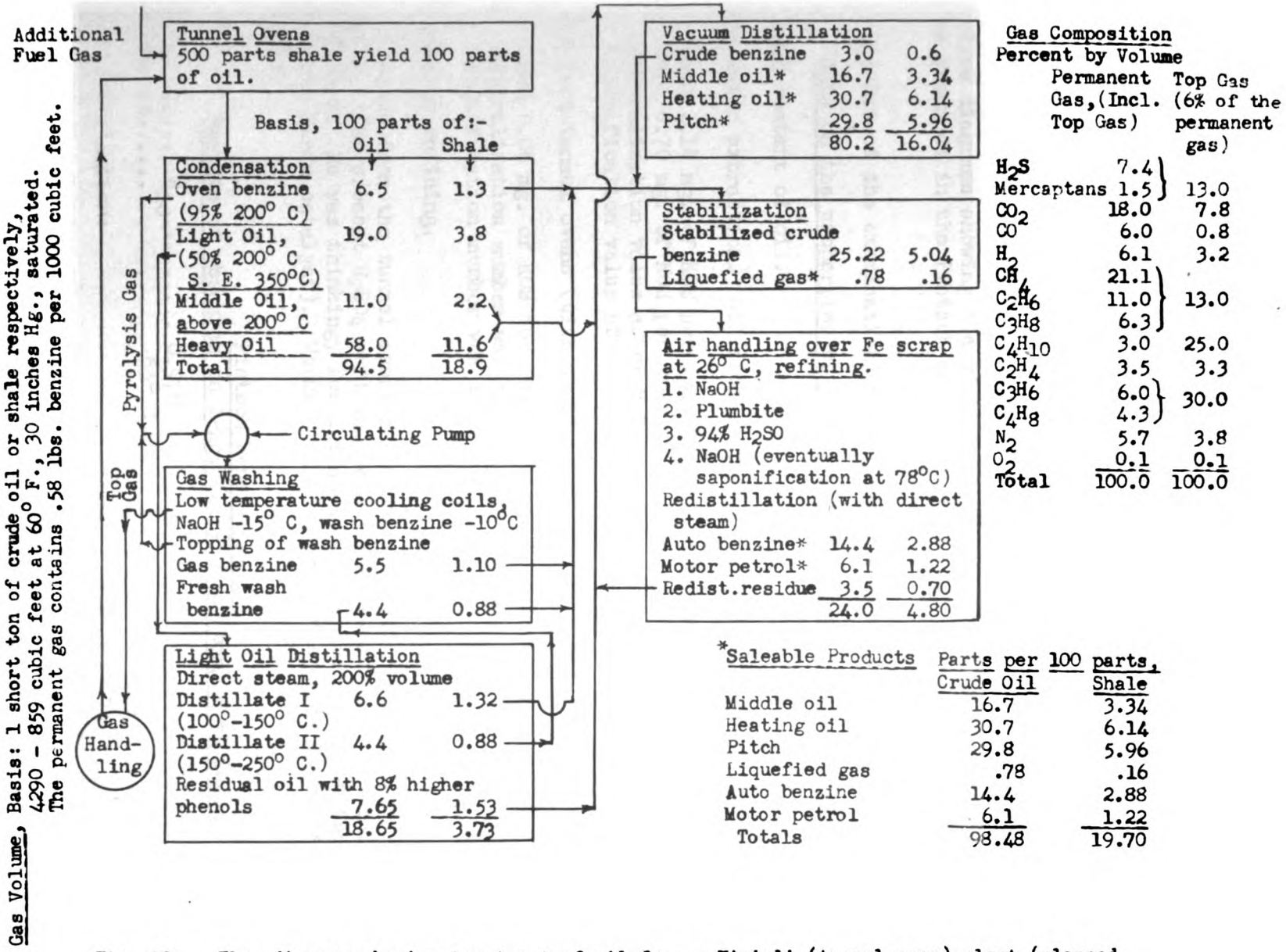
Additional Fuel Gas
Tunnel Ovens
500 parts shale yield 100 parts of oil.
Basis, 100 parts of:-
Oil
Shale
Condensation
Oven benzine (95% 200° C) 6.5 1.3
Light Oil, (50% 200° C S. E. 350°C) 19.0 3.8
Middle Oil, above 200° C 11.0 2.2
Heavy Oil 58.0 11.6
Total 94.5 18.9
Pyrolysis Gas
Top Gas
Circulating Pump
Gas Washing
Low temperature cooling coils, NaOH -15° C, wash benzine -10°C
Topping of wash benzine
Gas benzine 5.5 1.10
Fresh wash benzine 4.4 0.88
Light Oil Distillation
Direct steam, 200% volume
Distillate I (100°-150° C.) 6.6 1.32
Distillate II (150°-250° C.) 4.4 0.88
Residual oil with 8% higher phenols 7.65 1.53
18.65 3.73
Gas Hand-ling
Vacuum Distillation
Crude benzine 3.0 0.6
Middle oil* 16.7 3.34
Heating oil* 30.7 6.14
Pitch* 29.8 5.96
80.2 16.04
Stabilization
Stabilized crude benzine 25.22 5.04
Liquefied gas* .78 .16
Air handling over Fe scrap at 26° C, refining.
1. NaOH
2. Plumbite
3. 94% H2SO
4. NaOH (eventually saponification at 78°C)
Redistillation (with direct steam)
Auto benzine* 14.4 2.88
Motor petrol* 6.1 1.22
Redist.residue 3.5 0.70
24.0 4.80
Gas Volume, Basis: 1 short ton of crude oil or shale respectively, 4290 - 859 cubic feet at 60° F., 30 inches Hg., saturated. The permanent gas contains .58 lbs. benzine per 1000 cubic feet.
Gas Composition
Percent by Volume
Permanent Gas,(Incl. Top Gas)
Top Gas (6% of the permanent gas)
H2S 7.4
Mercaptans 1.5 13.0
CO2 18.0 7.8
CO 6.0 0.8
H2 6.1 3.2
CH4 21.1
C2H6 11.0 13.0
C3H8 6.3
C4H10 3.0 25.0
C2H4 3.5 3.3
C3H6 6.0 30.0
C4H8 4.3
N2 5.7 3.8
O2 0.1 0.1
Total 100.0 100.0
*Saleable Products
Parts per 100 parts, Crude Oil
Parts per 100 parts, Shale
Middle oil 16.7 3.34
Heating oil 30.7 6.14
Pitch 29.8 5.96
Liquefied gas .78 .16
Auto benzine 14.4 2.88
Motor petrol 6.1 1.22
Totals 98.48 19.70

Fig. 20. - Flow diagram showing treatment of oil from a Kivioli (tunnel-oven) plant (planned vacuum distillation).

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Product Refining and Properties of the Products

The first primitive "work-up" consisted in separating an automobile fuel (fraction up to 200° C.), the remainder being used as fuel oil. At Kivioli, where tunnel ovens are employed, a careful fractional condensation and gas washing for better benzine yields was carried out. This system called for a thoroughly modern product work-up.

In the newly planned expanded Works 6 there were to be centralized facilities for benzine refining.

Flow diagrams showing the yields and separation of products from shale oil as produced in the Pintsch and tunnel ovens are shown in figures 19 and 20.

Results of the examination of the products were as follows:

Data on the properties of the oil and treatment of the benzine

1. Acid content of oil.

Hot-water extraction. Oil from Pintsch ovens (without heavy oil):

Used 1.14 mg. of KOH per gram of oil for neutralization of H_2SO_4.
Used 0.70 mg. of KOH per gram of oil for neutralization of HCl.
Neutralization value after H_2O extraction was 1.3 mg. of KOH.
Saponification value after H_2O extraction was 1.8 mg. of KOH.

Oil from tunnel ovens (without light oil and benzine):

Used 0.06 mg. of KOH for neutralizing mineral acids.
Neutralization number was 3.9.
Saponification number was 19.5.

2. Benzine refining.

Benzine from the tunnel ovens has a neutralization number of 64-66 before refining. The present H_2SO_4 refining method must be changed, according to Dr. Winkler. He was thinking, for instance, of the Rostin method (benzine vapor over Fe-Cu catalyst). Works 6 will later be the centralized benzine refinery.

Pintsch generator oil.
Results of research on 1-kg. (2.2-pound) sample at Leuna

Density.....d_{20}..... 0.978
Flash point..... 63° C.

Engler distillation:

Temperature, ° C.	98	150	200	220	240	260	280	300	320	340	360
Percent off by volume	2.6	7.4	12.2	15.4	19.6	24.5	27.2	35.4	42.8	57.8	

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Distillation with a 30-centimeter (11.8-inch) column:

Benzine to 200° C.	Above 200° C.	Water	Loss
9.15	89.6	0.7	0.55 percent by weight

Elementary analysis:

	Percent
Carbon	81.85
Hydrogen	10.05
Nitrogen	0.40
Sulfur	1.20
	93.50

Dissolved water, percent	0.7
Treatment with 15 percent NaOH showed, percent by weight of acidity	5.13
Treatment with 10 percent Na_2CO_3 showed, percent by weight of acidity	1.13
Hard asphalt content, percent by weight	7.56
Soft asphalt content, percent by weight	0.0
Benzine, up to 200° C., percent by weight	9.15

Engler distillation of benzine fraction:

Temperature, ° C.	98	110	120	130	140	150	160	170	180	190	200	R.
Percent off by volume	0.5	2.0	7.0	30	47	55.5	70	83	92	98.5	1.1	

Density d_{20}	0.800
Aniline point, ° C.	+8.80
Olefines and aromatics, percent	75.4
Olefines (Br. No.), percent	56
Residue from vaporization in a glass dish, mg	56

Rapid darkening after distillation.

Oil boiling above 200° C.

	Pour point, °C.	Olefines and aromatics, percent	Olefines, percent	Percent of crude oil by weight
Residue at 200° C. (original)	-18	-	-	91
Fraction 200°-250° C. (vac. dist.)	-48	73	60	6-7
250°-300° C. (" ")	-28	80	73	10
300°-350° C. (" ")	-13	94	76	10

Gas oil: (per year):

	Metric tons	Short tons	
Works 1	164,000	180,400	
Works 3	165,000	181,500	
Works 6	210,000	231,000	
Total	539,000	592,900	oil
from	2,700,000	2,970,000	shale
or	340	374	per hour.

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The amount of C_3 - C_4 hydrocarbons in gas from the tunnel ovens (permanent gas including top gas) is equivalent to 14,000 metric tons (15,400 short tons) per year.

Byproducts:

(a) Gas oil.

Analyses, carried out in London, of the permanent gas (including top gas) as well as that of the top gas alone were used as bases to obtain an idea of the amount of gas oil that may be recovered. No analysis was available of the very dilute Pintsch oven gas. In view of the very small production capacities for liquefied gas from each individual plant, the three largest works, 1, 3, and 6, were considered in common. These should produce 539,000 metric tons (593,000 short tons) of oil from 2,700,000 metric tons (2,970,000 short tons) of shale per year. From the planned combination it was anticipated that the permanent gas (including top gas) from the tunnel ovens would yield a total amount of C_3 and C_4 hydrocarbons equal to 14,000 metric tons (15,400 short tons) per year without including the stabilization gas. It was further anticipated that Works 3 and 4 would yield an additional 3,000 metric tons (3,300 short tons) of C_3 and C_4 hydrocarbons from the stabilization of the gas from both oven systems.

If the liquefied gas was obtained only from the concentrated top gas and stabilizer gas, the above 17,000 metric tons (18,700 short tons) would have to be reduced to 2,750 + 3,000 = 5,750 metric tons per year (3,030 + 3,300 = 6,330 short tons per year).

If the plants consisted only of tunnel ovens, these C_3 and C_4 hydrocarbon totals would be increased by about 32,000 metric tons (35,200 short tons) per year, that is, by 10,000 metric tons (11,000 short tons) in the top gas and stabilizer gas.

Fifty to sixty percent of the C_3 - C_4 hydrocarbons are olefines (see analyses). These can be converted to polymerbenzine. It is also possible to recover all these olefine hydrocarbons in the order of magnitude present in the original material.

Thus, from a 100-metric ton (110-short ton) tunnel-oven installation an additional 0.5 metric ton (0.55 short ton) polymerbenzine and about the same amount of bottle gas can be obtained.

(b) Acetone could be obtained from the carbonization water from tunnel ovens at Kivioli. If the primitive purification methods described for obtaining pure acetone were efficient, the planned oven combination should yield about 150 metric tons (165 short tons) of acetone per year (containing about 0.05 percent of the crude oil) from the tunnel ovens, Pintsch-oven carbonization waters (condensates) are generally poor in acetone content. There should also be recovered 150 metric tons (165 short tons) per year of C_4 - C_5 ketones (called buton) and 75 metric tons (82.5 short tons) per year of higher ketone oils. Not included but fairly large amounts of acetone should also be found in the calcium chloride solutions used for cooling the tunnel-carbonization gases. If the planned 590,000 metric tons (649,000 short tons) of oil were obtained by tunnel ovens, then the above acetone figure must be doubled.

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(c) Phenols can be obtained in benzine refining (saturation of the NaOH solution with CO_2). These consist of 40 percent cresols, 60 percent xylenols, but no carbolic acid. The total amount recoverable should be 250 to 300 metric tons (275 to 330 short tons) per year (0.3 to 0.4 percent of the crude benzine). The phenol content of the sewage has not been determined but should be small.

The flow diagrams for Works 1 and 4 are shown in figures 21 and 22.

The construction of additional facilities for extraction of shale oil in Estonia was greatly retarded and (until the spring of 1943) no additional technical data were obtained, with the exception of analyses and inspections. These analyses were carried out on larger samples furnished by the Estonian firm. German technicians visited the installations in November 1942 and made a fairly comprehensive report. The analyses reported on October 13, 1942, were carried out on larger samples and are probably more accurate. The results are tabulated below:

PROPERTIES OF ESTONIAN SHALE OIL I (FROM THE PINTSCH GENERATOR)

Original sample:

Density..... d_{20}	0.978
A.P. (cannot be determined; too dark)	
Flash point, ° C.....	63

Engler distillation:

Temperature, ° C.	98	150	200	220	240	260	280	300	320	340	360
Percent off by volume	2.6	7.4	12.2	15.4	19.6	24.5	27.2	35.4	42.8	57.8	

Distillation in a 30 cm. (11.8 inch) column:

	Benzine (to 200°C.)	Residue above 200°C.	H_2O	Loss
Percent by weight.....	9.15	89.60	0.70	0.55

Elementary analysis:

	Percent
Carbon.....	81.35
Hydrogen.....	10.05
Nitrogen.....	.40
Sulfur.....	1.20
	93.50

Dissolved water, percent.....	0.70
Acid oils (with 15 percent NaOH), percent by weight.....	5.13
Acid oils (with 10 percent Na_2CO_3), percent by weight.....	1.13

(Note that acid-oils content is identical with the previously reported results.)

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Total Throughput of Shale 2507 Short Tons Per Day

All data is given on a basis of 1 day's production. The units are short tons except as otherwise noted.

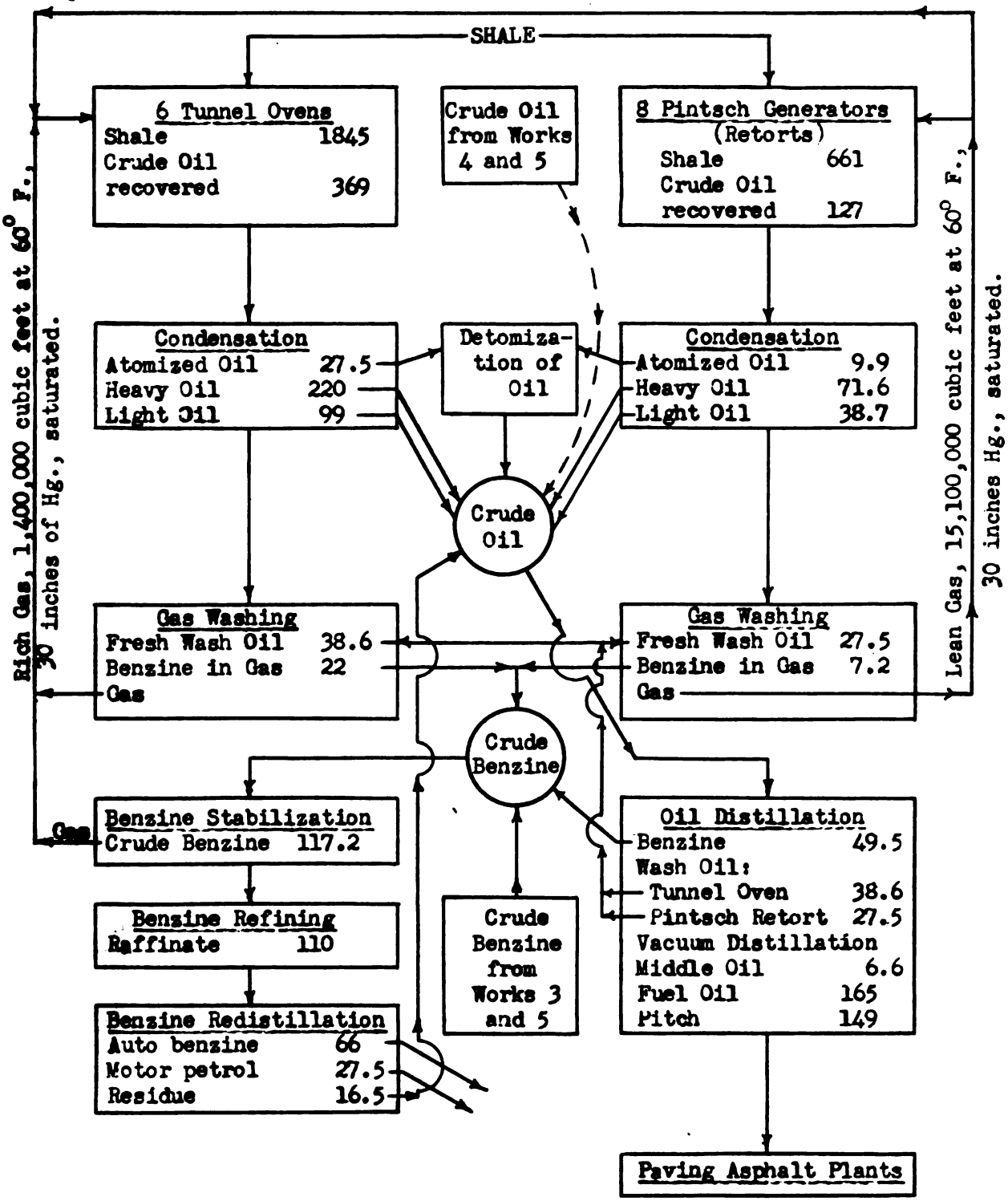

Fig. 21. – Flow diagram of Works No. 1 (Kivioli), treating shale by both the tunnel ovens and the Pintsch retorts.

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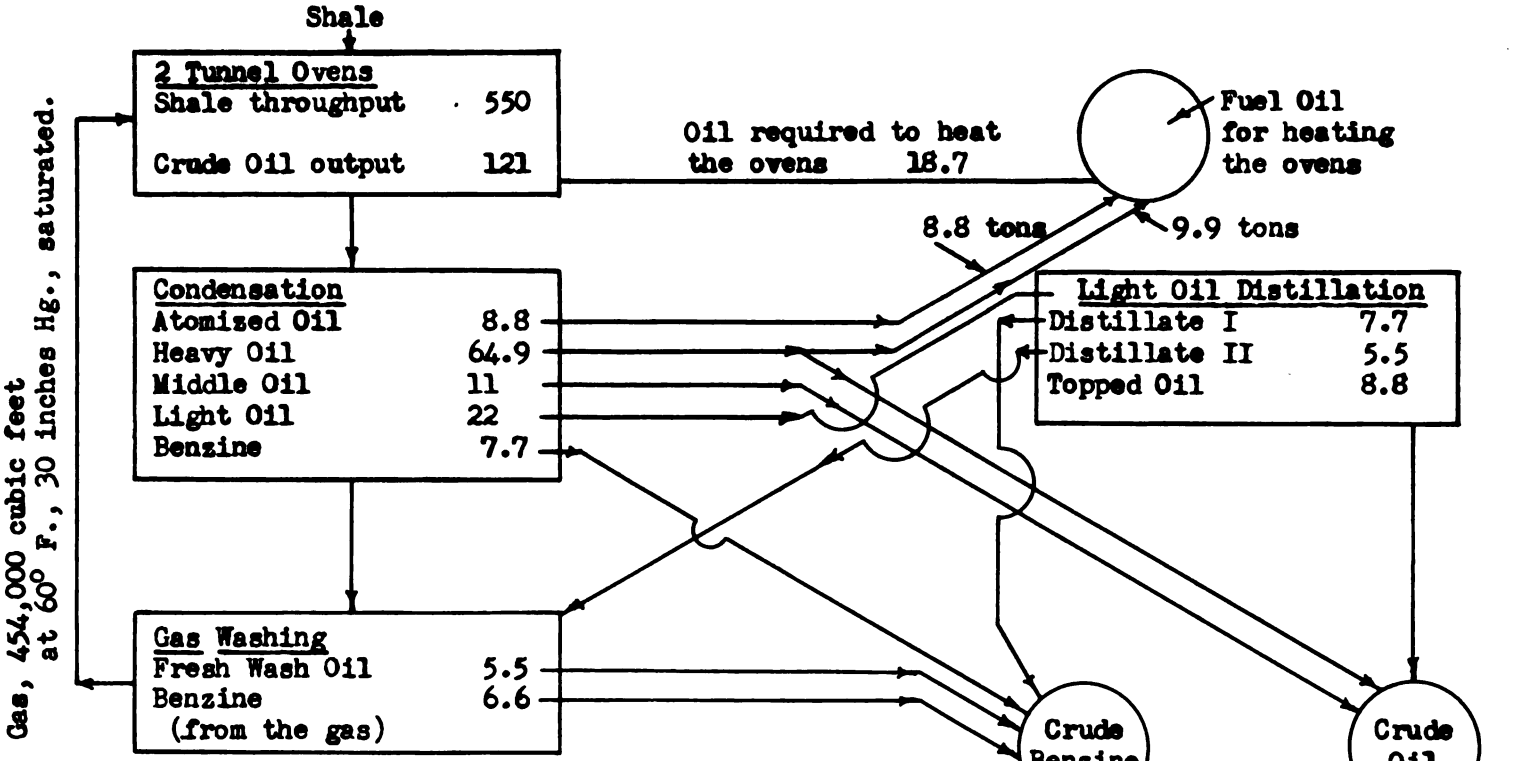
All data is on a basis of 1 day's production. The units are short tons except as otherwise noted.



Overall Production	
Heavy Oil	55
Middle Oil	11
Benzine and Light Oil	24.2
Benzine from Gas Washing	6.6
Total Saleable Products	96.8
Fuel Oil for heating the Ovens	9.9
Fuel from atomized Oil, also used for heating the Ovens	8.8
Fresh Wash Oil	5.5
Total	121

Fig. 22. - Flow diagram of Works No. 4 (Sillama), treating oil from tunnel ovens.

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Distillation in a column 1 meter (39.37 inches) long:

	Percent by volume
Water	4.5
Benzine up to 200° C.	1.0
Fraction (vacuum dist.):	
200°-250° C.	9.2
250°-300° C.	6.5
300°-350° C.	9.6
350°-380° C.	9.9
Total distillate	40.7
Residue	57.0
Gas and loss	2.3
	100.0

Properties of the benzine fraction distilling up to 200° C.:

Density d_{20}	0.800
A.P., ° C.	+8.8
Olefines and aromatics (100 percent H_2SO_4), percent	75.4
Bromine No.	71.2
Iodine-thiocyanogen No.	93.8
Olefines, percent	56
Glass dish gum residue, mg.	56
Acid oils, percent by weight	2.47

Engler distillation:

Temperature, ° C.	98	120	140	160	180	200	Residue
Percent off by volume	2.0	30.0	55.5	83.0	98.5		1.1

The benzine is brownish-red.

Elementary analysis:

	Percent
Carbon	84.18
Hydrogen	12.65
Sulfur	1.47
	98.30

Properties of fractions over 200° C.:

Fraction: temperature range, ° C.	Density d_{20}	A.P., ° C.	Pour point, ° C.	Aromatics and olefines, percent	Bromine No.	Iodine-thiocyanogen No.
200-250	0.860	+18.8	-51	73.0	51	-
250-300	.919	+25.0	-28	80.6	50	79.6
300-350	.985	-7.2	-6	94.0	38	-
350-365	1.009	-20.0	+5	97.0	41	63

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Some of the crude oil was topped at 200° C. and freed from phenols and asphalts by diluting with a light benzine and shaking with caustic-soda solution. An oil boiling above 200° C. can be separated from the crude to the extent of 45 percent by distillation; consequently, if the 10-percent benzine is included, about 55 percent of the crude oil can be recovered.

Properties of the phenol and asphalt-free fraction 200°-400° C.:

Density.....d_{20}.....	0.923
Pour point, ° C.....	3.2
Olefines and aromatics, percent.....	85.4
Bromine No.....	44.8

Engler distillation:

Temperature, ° C.	218	240	280	300	340	380	400	405	Residue
Percent off by volume	9.0	30.0	38.0	55.0	76.0	91.0	97.0		2.6

PROPERTIES OF ESTONIAN SHALE OIL II (FROM TUNNEL RETORTS)

Original sample:

Density.....d_{20}.....	0.930

Engler distillation:

Temperature, ° C.	130	140	160	180	200	220	240	260	280
Percent off by volume	0.1	0.15	2	4	7	10	14.3	18.4	24

Temperature, ° C.	300	320	340	360	365	370	Residue
Percent off by volume	29.2	36.4	48	68.4	76.3	86.1	Solid

A.P. too dark to determine.	
Flash point, ° C.....	89
Water content, percent.....	1.9-1.95
Acid oils with 15 percent NaOH, percent by weight.....	14.195
Acid oils with 10 percent Na_2CO_3, percent by weight....	1.275
Acid in water, percent.....	.318
Olefines and aromatics (100 percent H_2SO_4), percent....	96.2
Bromine No.(about 36 percent olefines when mol. weight is 250).....	23.9
Hard asphalt, percent.....	8.11

Elementary analysis:

	Percent
Carbon.....	82.00
Hydrogen.....	9.90
Nitrogen.....	0.58
Sulfur.....	1.03
	93.51

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Fractionation of the shale oil gave:

	Percent
Water	2
Benzine to 200° C.	10
Oil (200°-430° C., vacuum dist.)	45
Asphalt[a]	38
Loss[b]	5
	100

a/ Still contains oil that was not distilled to decomposition.

b/ The high loss figure is due to the asphaltic residue, which could not be entirely collected.

The 200° to 430° C. fraction was distilled in vacuum and further fractionated. A fraction boiling between 230° and 340° C. (26 percent by volume of the charge) and another boiling at 200° to 300° C. were especially studied.

Properties of benzine, fraction up to 200° C.:

Density.....d_{20}	0.759
A.P., ° C.	+27.1
Bromine No.	25.7
Aromatics and olefines (24 percent olefines when mol. weight is assumed to be 140), percent	59.9
Acid oils, percent	0.132

Engler distillation:

Temperature, ° C.	74	100	120	140	160	180	190	210	Residue
Percent off by volume	15.5	49.5	71.5	81.5	90.5	95.5	98.0		1.4

Elementary analysis:

	Percent
Carbon	84.75
Hydrogen	13.44
Nitrogen	.11
Sulfur	.90
	99.20

Properties of the fraction 230° to 340° C. (26 percent by volume of original sample):

Density.....d_{20}	0.917
A.P., ° C.	+29.9
Aromatics and olefines, percent	66.2
Bromine No.	27.3
Iodine-thiocyanogen No.	37.8
Acid oils, percent	10.4

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Engler distillation:

Temperature, °C.	232	260	280	300	320	330	339	Residue
Percent off by volume	3.0	31.5	67.0	81.0	86.0	98		1.5

Elementary analysis:

	Percent
Carbon	84.76
Hydrogen	11.20
Nitrogen	.38
Sulfur	.82
	97.16

An average molecular weight of 210 is equivalent to 36 percent olefines.

Properties of fraction 200° to 300° C.:

Density d_{20}	0.862
A.P., °C.	+38.3
Bromine No.	19.0
Aromatics and olefines (100 percent H_2SO_4), percent	52.7
Acid oils, percent	4.05

Engler distillation:

Temperature, °C.	208	220	240	260	280	293	Residue
Percent off by volume	3.5	39	81	94	97.5		2

Elementary analysis:

	Percent
Carbon	85.40
Hydrogen	12.27
Nitrogen	.14
Sulfur	.88
	98.69

Properties of fraction 200° to 300° C. after washing with 20 percent H_2SO_4 and 15 percent NaOH solutions:

Density d_{20}	0.846
A.P., °C.	+38.1
Bromine No.	23.0
Aromatics and olefines (100 percent H_2SO_4), percent	50.1

Engler distillation:

Temperature, °C.	220	230	240	250	260	270	280	288	Residue
Percent off by volume	8.0	35.0	63.0	79.0	89.0	94.0	98.5		1.3

Elementary analysis:

	Percent
Carbon	85.46
Hydrogen	12.69
Sulfur	.89
	99.04

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